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# Metal Behavior in Acid Sulfate Soils of Thailand.

Philip Alderson Moore Jr

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**Metal behavior in acid sulfate soils of Thailand**

**Moore, Philip Alderson, Jr., Ph.D.**

**The Louisiana State University and Agricultural and Mechanical Col., 1987**

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Metal Behavior in Acid Sulfate Soils of Thailand

A DISSERTATION

Submitted to the Graduate Faculty of the  
Louisiana State University and  
Agricultural and Mechanical College  
in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy  
in the department of

Marine Sciences

by

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May 1987

In Memory of P. A. Moore  
(1917-1985)

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## ABSTRACT

Metal availability and uptake by rice in flooded acid sulfate soils from the Central Plains region of Thailand were evaluated under field, growth chamber and greenhouse conditions.

The results found in this study indicated that  $\text{Fe}^{2+}$  activities are seldom in equilibrium with pure Fe solid phases in these soils. This was believed to be due to (1) transient redox conditions, (2) the presence of ill-defined ferric oxides, and/or (3) cation exchange reactions. Equilibria calculations also indicated that these soils were undersaturated with respect to most Ca, Mg, and Mn solid phases, and their activities were believed to be controlled by cation exchange. The  $\text{Al}^{3+}$  activities were very pH dependent and appeared to be controlled by gibbsite at low pH and amorphous  $\text{Al}(\text{OH})_3$  at high pH. Zinc activities were also negatively correlated with pH, with many of the soil solutions supersaturated with respect to franklinite. Cupric copper ( $\text{Cu}^{2+}$ ) activities were positively correlated with pe, with cuprous ferrite indicated as the stable solid phase. Molybdate ( $\text{MoO}_4^{2-}$ ) activities were positively correlated with pH and appeared to be controlled by wulfenite. Borate ( $\text{B}(\text{OH})_3^0$ ) activities were highly correlated with ionic strength.

Leaf analysis indicated that Fe uptake was correlated with  $\text{Fe}^{2+}$  activity, however, a better relationship was found between uptake and  $E'-\text{Fe}$  (the divalent charge fraction in solution due to  $\text{Fe}^{2+}$ ). Calcium, Mg and Mn uptake was also found to be more closely related with  $E'-\text{Ca}$ ,  $E'-\text{Mg}$ , and  $E'-\text{Mn}$  than with the activities of these ions. Although Al uptake was not correlated with  $\text{Al}^{3+}$  activity, P uptake was, possibly due to variscite precipitation. Copper and Mo uptake was significantly



correlated with the activities of  $\text{Cu}^{2+}$  and  $\text{MoO}_4^{2-}$ , however, Zn uptake was not related with  $\text{Zn}^{2+}$  activity. The results of this study also indicated that Fe and Al toxicities and Ca, Mg, and Si deficiencies may occur on these soils.

Multiple correlation between soil parameters and growth indices indicated that the two most important variables affecting rice growth on these soils were  $\text{E}'\text{-Fe}$  and pH. While  $\text{E}'\text{-Fe}$  was considered to be a measure of Fe stress (Fe toxicity combined with basic cation deficiencies), pH measurements reflected the availability of many nutrients and toxins, such as P and Al.

## Preface

During the past 25 years the "Green Revolution" has resulted in increased rice yields in many third world countries and has been a boon for mankind. However, due to population increases in many of these countries, the specter of widespread hunger looms as ominously on the horizon today as it did in the 1960's. Therefore, a concerted effort is needed to keep increases in food production abreast with the population explosion.

Problem soils are one of the primary stumbling blocks to increased rice yields in many areas of the world. In Asia, where a large part of the diet is rice, the main problem soils have been identified as saline, sodic, peat and acid sulfate soils; with 5.4 million hectares of the latter occurring in South and Southeast Asia alone.

Acid sulfate soils are formed in coastal regions where large quantities of pyrite ( $\text{FeS}_2$ ) accumulate in intertidal sediments. Pyrite accumulation in these sediments is a result of anaerobic conditions, which cause sulfate from seawater to be reduced to sulfides and ferric iron from iron oxides to be reduced to ferrous iron. A large part of the alkalinity formed during sulfate reduction is flushed from the sediments by tidal action, leading to a potentially acid soil. If these soils are aerated, either by natural or artificial drainage, then pyrite is oxidized, releasing sulfuric acid and iron. The acidity resulting from this process causes soil physico-chemical conditions which are extremely detrimental to plant growth.

Among the primary disorders of plants growing on acid sulfate soils are metal toxicities. Due to the acidic nature of these soils, metals such as  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  often build up in the soil solution until they

reach toxic proportions. Although heavy applications of  $\text{CaCO}_3$  or other liming materials can alleviate metal toxicities on these soils, amendments of this kind are generally cost prohibitive. In order to develop management strategies that are cost effective, information concerning soil-plant relationships is needed. Therefore, the objectives of this research were: (1) to determine the availability of metals in acid sulfate soils, (2) to determine the relationships between soil physico-chemical parameters and metal availability, (3) to determine the relationships between metal availability and uptake by rice, and (4) to determine the effects of metal availability and other soil physico-chemical parameters on rice growth in these soils.

In order to meet these objectives, three experiments were conducted on acid sulfate soils from the Central Plains region of Thailand. Since the methodology and results of the experiments were similar, I have chosen to organize this dissertation by metals or groups of metals. This was done to keep redundancy to a minimum.

The scope of the different sections is as follows:

Chapter 1 provides an introduction to acid sulfate soils, with particular reference to those occurring in the Central Plains of Thailand.

Chapters 2-6 concern metal availability and uptake by rice in acid sulfate soils. The principal theme of these chapters revolves around the geochemistry of metals. Metal activities were calculated with the best available means, and mechanisms of metal control were explored. Furthermore, the relationships between metal activities and uptake by rice were investigated.

Chapter 7 deals with the effect of metal availability and other soil physico-chemical parameters on the growth of rice. Using simple and multiple correlation techniques, the key edaphic agents believed to be governing rice growth on these soils were determined and the extent of their influence was delineated.

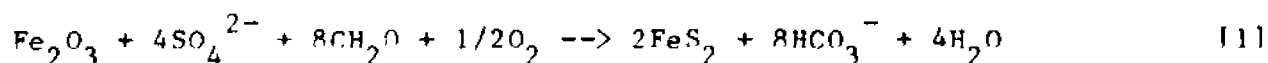
Appendix I is devoted to current agricultural management practices used to produce rice in the Central Plains region of Thailand. This section was included solely to enlighten readers on the conditions and logistics of rice production in Southeast Asia.

Chapter One  
Introduction to Acid Sulfate Soils

## Introduction

Actual and potential acid sulfate soils are found on an estimated 12.5 million hectares of land throughout the world (FAO/UNESCO, 1979). These soils usually occur on low-lying coastal lands in the tropics, with large areas located in South and Southeast Asia, Africa, and South America. In the Central Plains region of Thailand there are over 900,000 hectares of acid sulfate soils, of which about 95% is cultivated in rice (Charoenchamratcheep et al., 1982). Due to their acidic nature, crop production is often severely limited on these soils.

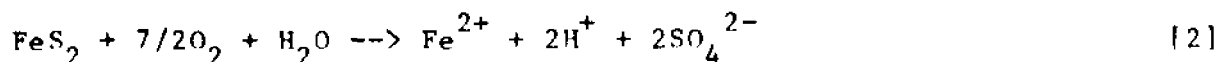
The first stage of acid sulfate soil formation involves the production of pyrite (sulfidation), which occurs in clayey intertidal environments such as mangrove swamps where tidal flushing is strong. The necessary prerequisites for pyrite formation are (1) sulfate, (2) sulfate reducers, (3) organic matter, (4) iron, and (5) alternate periods of anaerobic and aerobic conditions (Pons and Van Breeman, 1982). The sulfate is derived from seawater, the iron from iron oxides and clays, and the organic matter from mangroves and reeds growing in adjacent areas. The organism responsible for sulfate reduction is Desulfovibria desulfuricans. As sulfide is formed in these reduced sediments, it reacts with ferrous iron to form FeS (mackinawite). During periods of low tide, some of the sulfide is partially oxidized to  $S^0$  (elemental sulfur) which reacts with FeS to form  $FeS_2$  (pyrite). The overall reaction for this process can be written as follows;



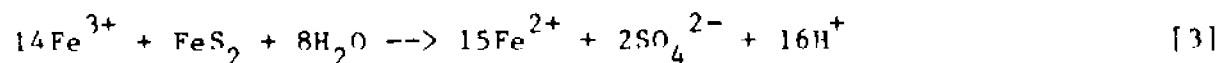
The bicarbonate formed is then leached out of the system by tidal flushing, leaving pyrite, which is a form of potential acidity. Acidity due to pyrite oxidation can only occur when this alkalinity is removed and the sediments are low in calcium carbonate. Since calcium carbonate contents are generally low in the humid tropics and high in temperate regions (often higher than 10%), acid sulfate soil formation occurs almost exclusively in tropical environments (Pons et al., 1982).

The second major step in the formation of acid sulfate soils involves aeration of the pyritic sediments, which leads to pyrite oxidation and subsequent acid formation (sulfuricization). Aeration can be brought about by natural or artificial drainage. In Thailand, natural drainage has been caused by a slight upward tilting of the Bangkok Plain in recent geologic time, combined with a decrease in the relative sea level (Van Breeman, 1976). In the later half of the 1800's, drainage was accelerated by the digging of a network of canals (locally referred to as klongs) throughout the NE portion of the Bangkok Plain for transportation and improved water diversion.

Immediately following drainage, the pH of these soils is near neutrality and the primary route of pyrite oxidation begins as  $O_2$  enters the soil, as follows;



This reaction is not pH dependant and may or may not be microbially mediated. As it proceeds, the production of  $H^+$  ions causes a decrease in pH. Under conditions of low pH and high Eh, an alternate route of pyrite oxidation involving  $Fe^{3+}$  is initiated as follows;



This route of pyrite oxidation is pH dependant and microbially mediated. The genus of bacteria primarily involved in the oxidation of pyrite is Thiobacillus. These chemo-autotrophs utilize S as an energy source and reduce  $\text{CO}_2$  for a C source. The three species of Thiobacillus responsible for pyrite oxidation in the formation of acid sulfate soils are: (1) T. Ferrooxidans - which oxidize  $\text{Fe}^{2+}$ ,  $\text{FeS}_2$ , and  $\text{S}^0$ , (2) T. thiooxidans - which oxidize  $\text{FeS}_2$  and  $\text{S}^0$ , and (3) T. acidophilus - which oxidize  $\text{S}^0$  (Nordstrom, 1982).

Under conditions of low pH-high Eh, pyrite oxidation by  $\text{Fe}^{3+}$  is much faster than by  $\text{O}_2$  and is a self perpetuating process. The rate at which this process occurs is dependent upon the concentration of  $\text{Fe}^{3+}$  in solution, which is controlled by the rate of  $\text{Fe}^{2+}$  oxidation. Although inorganic  $\text{Fe}^{2+}$  oxidation does occur, it is 5 or 6 orders of magnitude slower than microbial oxidation (Nordstrom, 1982). This implies that the amount of  $\text{FeS}_2$  oxidized in one day by this process in the presence of microorganisms would be equivalent to that oxidized in a sterile system over a period of several hundred to several thousand years.

One of the primary oxidation products of pyrite is  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  (jarosite). This mineral causes the conspicuous yellow mottles in acid sulfate soils that resulted in the term "Cat Clays", which is often used in conjunction with these soils. Jarosite formation occurs under low pH-high Eh conditions, where  $\text{SO}_4^{2-}$  concentrations are high and in the presence of  $\text{K}^+$ . Other sulfate bearing minerals that may occur in acid sulfate soils are  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum),  $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (alum),  $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (tamarugite),  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  (rozenite),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (melanterite),  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  (szomolnokite),  $\text{Fe}_5(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$  (copiapite) and  $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$  (alunite) (Nordstrom, 1982). Van Breeman



(1973a) also indicated the possible existence of  $\text{AlOH}\text{SO}_4$  (basic aluminum sulfate) in these soils.

With time and adequate rainfall, the sulfuric acid produced by pyrite oxidation leaches downward through the soil profile, causing the pH of the topsoil to increase. Under these conditions, jarosite becomes unstable and other iron minerals such as  $\text{Fe}(\text{OH})_3$  (amorphous iron hydroxide) and/or  $\text{FeOOH}$  (goethite) become the stable phase of iron. The presence of goethite in acid sulfate soils is denoted by the characteristic brown mottles formed by this mineral phase. Under extremely desiccating conditions, such as that found in the western portion of the Bangkok Plain, goethite can be transformed to hematite, which occurs as red mottles (Van Breeman, 1976).

Fortunately, acid sulfate soils are a transient phenomenon, due to leaching. As  $\text{H}_2\text{SO}_4$  and  $\text{K}^+$  move downward with time, the depth of jarosite becomes deeper. This process results in the profile development of these soils. A typical acid sulfate soil (Sulfic Tropaquept) has characteristic brown and red mottles from goethite and hematite in the A horizon, yellow mottles of jarosite in the B horizon and a dark grey reduced pyritic substratum in the C horizon as shown in Plate 1.

The profile development of acid sulfate soils is used in soil taxonomy to classify these soils. Strictly speaking, all acid sulfate soils are in the Inceptisol order and Aquept great group. The two main types of acid sulfate soils in Asia are Sulfic Tropaquepts and Typic Sulfaquepts. Sulfic Tropaquepts are defined by the USDA (1975) as soils that "either have jarosite mottles and a pH (1:1 water, air dried slowly in the shade) between 3.5 and 4.0 in some part within a depth of 50 cm,



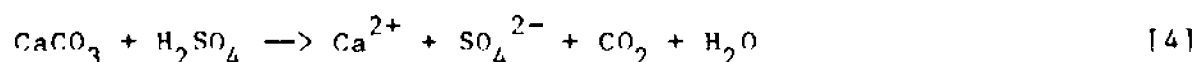
Plate 1. A typical acid sulfate soil (Sulfic Tropaquept) in the Central Plains region of Thailand.

or they have jarosite mottles and a pH (1:1 water, air dried slowly in the shade)  $< 4.0$  in some part between depths of 50 and 150 cm below the soil surface." Typic Sulfaquepts are defined as "Sulfaquepts that have a sulfuric horizon within 50 cm of the soil surface. The sulfuric horizon is composed either of mineral or organic soil material that has both a pH  $< 3.5$  (1:1 in water) and jarosite mottles (the color of fresh straw that has a hue of 2.5 Y or yellower and Chroma of 6 or more)". Whereas Sulfic Tropaquepts can support plant growth in an unaltered state, the Sulfaquepts are generally considered to be unsuitable for agriculture when unamended (Van Breeman, 1982).

Potential acid sulfate soils are of the Entisol order and Aquent great group. The most common mineral potential acid sulfate soils are the Typic Sulfaquents. The USDA (1975) defines these soils as "Sulfaquents that have sulfidic materials within 50 cm of the mineral soil surface if the  $n$  value is  $> 1$  or within 30 cm if the  $n$  value is  $< 1$ ," where sulfidic materials are defined as "waterlogged mineral or organic soil materials that contain 0.75 percent or more sulfur (dry weight), mostly in the form of sulfides and that have less than three times as much carbonate ( $\text{CaCO}_3$  equivalent) as sulfur." Upon oxidation, these soils become extremely acidic and virtually sterile.

The acidity that results from the oxidation of sulfidic materials in potential acid sulfate soils is neutralized and/or deactivated by several mechanisms. Van Breeman (1973b) stated that the three major fractions responsible for inactivating sulfuric acid in these soils are (1) solution alkalinity, (2) exchangeable bases, and (3) weatherable minerals.

The neutralization of sulfuric acid by carbonate alkalinity in solution is probably the first mechanism of inactivation that becomes operable in these soils. The reaction describing this process can be written as follows:



Based on the low alkalinity of interstitial waters in non-alkaline soils, Van Breeman (1973b) calculated that this process could, at best, neutralize only 1 meq of acid per 100 g of soil. However, he indicated that the pH of topsoils that had been periodically flooded with moderately alkaline waters, such as the western portion of the Bangkok Plain, may have increased markedly over the centuries due to this process.

The second mechanism by which acidity can be inactivated involves adsorption of  $\text{H}^+$  ions onto clays and organic matter. Under normal pH conditions this results in non-exchangeable  $\text{H}^+$  which provides the basis for the pH-dependent CEC, whereas truly exchangeable  $\text{H}^+$  is normally only present in measurable quantities below pH 4.0 (Bohn et al. 1979). Van Breeman (1973b) stated that between 5 and 10 meq of acid per 100 g of soil is adsorbed by the exchange complex of typical acid sulfate soils in Thailand when the pH drops from 7.5 or 7.0 to around 5.0.

The third mechanism in which acidity may be deactivated is by dissolution of weatherable minerals. This soil fraction encompasses a broad array of mineral phases, ranging from carbonates to clays. Therefore, the deactivation of acidity by this mechanism is dependant upon the types and amounts of weatherable minerals present. When carbonate contents are low, the other minerals such as montmorillonite

or kaolinite buffer the pH in these soils, resulting in acidic conditions.

The most important aspect of acidification in these soils is the influence it has on the availability of nutrients and toxins to plants. While the concentrations or activities of metals such as  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$  may reach toxic proportions under low pH conditions, the solubilities of certain essential nutrients such as phosphorus decrease, due to precipitation and/or adsorption phenomena. The net result of these processes is a decrease in plant growth and/or an increase in plant mortality.

In a review of the the literature concerning acid sulfate soils, Satawathananont (1986) listed the following problems associated with poor rice growth on these soils: (1) hydrogen toxicity, (2) aluminum toxicity, (3) iron toxicity, (4) sulfide toxicity, (5) electrolyte stress, (6) adverse effects of carbon dioxide and organic and inorganic acids, (7) phosphorus deficiency, (8) low base status, and (9) impaired microbial activities. However, several of these problems have yet to be documented in acid sulfate soils, raising questions as to their possible existence. The relative significance of those problems that have been documented in these soils is also lacking. Therefore, the overall objectives of this research were to study the availability of nutrients and toxins in acid sulfate soils and to determine the resulting impact of these parameters on paddy rice.

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## Chapter Two

### Iron Availability and Uptake by Rice in Acid Sulfate Soils

## ABSTRACT

Iron availability and uptake by rice was evaluated in 132 flooded acid sulfate soils in the Central Plains region of Thailand and in a growth chamber experiment utilizing 50 of the same soils. Soil and plant metal analyses were conducted at the panicle differentiation stage of growth in both studies and in the soil prior to transplanting in the growth chamber experiment. The R.D. 23 rice variety was used in the growth chamber study, while 88 different varieties (native and improved) were sampled in the field study. Metal activities in soil solutions were determined from free metal concentrations using GEOCHEM and activity coefficients using the Davies equation. Exchangeable metals were determined from sodium acetate extracts buffered to the soil pH.

The results presented in this chapter indicate that  $\text{Fe}^{2+}$  activities in flooded acid sulfate soils are seldom in equilibrium with pure Fe solid phases under natural conditions. This is believed to be due to (1) transient redox conditions, (2) the presence of ill-defined ferric oxides or hydroxides, and/or (3) cation exchange reactions.

Although leaf Fe contents were correlated with  $\text{Fe}^{2+}$  activities, a better relationship existed between leaf Fe and  $\text{E}'\text{-Fe}$ , indicating that ion competition may be important in determining Fe uptake in rice. The critical  $\text{E}'\text{-Fe}$  observed for Fe toxicity conditions was approximately 0.75. These findings clarify the role of other nutrients in Fe toxicity in rice.

Key words - Cation exchange,  $\text{Fe}^{2+}$  activity, Fe toxicity, GEOCHEM, mineral equilibria, flooded soils, Oryza sativa.



The redox chemistry of Fe in flooded soils has received a considerable amount of attention (Gotoh and Patrick, 1974; Patrick and Henderson, 1981a; Patrick and Henderson, 1981b; Ponnamperuma et al., 1967; Ponnamperuma et al., 1966; Schwab and Lindsay, 1983; Williams and Patrick, 1971). One reason for this interest is the dominating effect Fe has on the chemistry of flooded soils. Patrick and Reddy (1978) reported that the amount of Fe that can undergo reduction usually exceeds the total amount of other redox elements by a factor of ten or more.

Attempts to determine the solid phase of Fe controlling its solubility in aqueous systems have often met with limited success. Barnes and Back (1974) were unable to relate Eh, pH and dissolved  $\text{Fe}^{2+}$  with theoretical values assuming hematite or amorphous  $\text{Fe}(\text{OH})_3$  controlled  $\text{Fe}^{2+}$  solubility. Likewise, Olumu et al. (1973) were unable to relate theoretical  $E^0$  values for the  $\text{Fe}_2\text{O}_3$ - $\text{Fe}^{2+}$  redox system with experimental data. They concluded that a high degree of Fe complexing was the probable cause for this failure. In a field study with varying additions of O.M., Yoon et al. (1975) were unable to find a relationship between  $\text{Fe}^{2+}$  concentration in soil solution and  $\text{Eh}_7$ . In a study conducted under controlled pH and redox conditions, Gotoh and Patrick (1974) stated that  $\text{Fe}^{2+}$  in solution was governed by the  $\text{Fe}^{2+}$ - $\text{Fe}(\text{OH})_3$  system in which the ferric oxyhydroxide was a mixture of goethite and amorphous material.

Van Breemen (1969) indicated that the equilibria between ferric and ferrous iron were governed largely by ill-defined ferric oxides, which were intermediate between amorphous  $\text{Fe}(\text{OH})_3$  and goethite as far as stability is concerned. This was supported by Langmuir and Whittemore

(1971) who demonstrated that naturally occurring ferric oxyhydroxides were usually mixtures of x-ray amorphous material and goethite, with apparent activity products ranging from 37.3 for the amorphous form to 43.3 for the crystalline form.

Ponnamperuma (1972) reported that soil solutions were commonly supersaturated with respect to siderite ( $\text{FeCO}_3$ ). Schwab and Lindsay (1983) found that siderite controlled  $\text{Fe}^{2+}$  solubility in one Colorado soil if the  $\text{pe} + \text{pH}$  was below 8.5. They also indicated that  $\text{Fe}_3(\text{OH})_8$  (ferrosic hydroxide) controlled  $\text{Fe}^{2+}$  above  $\text{pe} + \text{pH}$  of 8.5.

Studies conducted on Fe availability to rice have often shown that uptake was related to solubility (Schwab and Lindsay, 1983; Tanaka et al., 1966; Yoon et al., 1975). Ponnamperuma et al. (1955) stated that Fe toxicity was the probable cause of a physiological disease of rice found in highly reduced paddy fields. This was confirmed by Tanaka et al. (1966) who showed that high levels of Fe in nutrient solutions led to elevated plant concentrations and to Fe toxicity symptoms. Later work by Tanaka and Naverso (1966a) suggested that decreases in Fe uptake were associated with increases in Mn uptake. Several workers have indicated that Fe toxicity in rice is the result of a multiple nutritional stress which occurs in plants with low levels of K, P, Ca and Mg (Benckiser et al., 1984a; Benckiser et al., 1984b; Howeler, 1973; Ottow et al., 1983). Iron toxicity has been implicated as the main cause of poor growth of lowland rice on acid sulfate soils (Tanaka and Naverso, 1966b).

The objectives of this study were: (1) to determine the activity of  $\text{Fe}^{2+}$  in flooded acid sulfate soils under natural conditions, (2) to determine what controls  $\text{Fe}^{2+}$  activity in these soils, and (3) to

determine the relationship between soil parameters and Fe content in rice.

## METHODS AND MATERIALS

### FIELD STUDY

Field sampling for this study was conducted between May and September in 1984 in the Central Plains region of Thailand. One hundred thirty four paddy fields characterized as Sulfic Tropaequents, Typic Sulfaequents, Typic Sulfaequents and Typic Tropaequents on farmers' fields and at research stations were sampled at the panicle differentiation (P.D.) stage of growth. Selection of sample sites was based on a newly revised map of the acid sulfate soils of Thailand (Osborne, 1984). Each site was visited several months prior to sampling in order to question farmers on planting dates and varieties, so that dates of P.D. could be estimated. The P.D. stage of growth has been recommended as the best time for collection of rice tissue samples for analysis (Mikkelsen, 1970). Approximately 88 different rice varieties were sampled in this study. Yield data from the previous year were also obtained from the farmers at this time.

Each site was visited at the estimated date of P.D. and ten plants were randomly selected from the field. The plants were sectioned longitudinally and the stage of growth was determined by visual inspection of the developing panicle. Fields were sampled only when the developing panicle was visible, but less than 2 cm in length. Several visits to each field were often required in order to sample at the specified growth stage.

After determining if the plants were at the appropriate stage of growth, an 'average' location was picked in the field and all of the aboveground plant parts were removed from a  $0.25\text{m}^2$  area and placed in plastic bags. Soil cores (20 cm I.D.) were taken to a depth of 20 cm with a stainless steel bucket auger and placed in plastic buckets of roughly the same diameter. A small amount of flood water was added in order to maintain flooded conditions. The soils sampled in this study had usually been flooded from six to eight weeks.

#### PLANT SAMPLES

Upon return from the field, the Y-leaves of the plants were separated, washed with deionized water and dried at  $70^\circ\text{C}$  in cotton bags. The Y leaf (most recently fully expanded leaf blade) has been recommended as the best leaf to examine for tissue analysis of rice (Westfall et al., 1973). A preliminary study on grinding methods indicated that the use of a Wiley mill led to significant Cu and Fe contamination, therefore plant samples were cut into small ( $<2\text{mm}$ ) pieces with stainless steel scissors for acid digestion. Digestion was accomplished in a 3:1 nitric to perchloric acid mixture. Soil contamination of the plants was evaluated by Ti analysis (Cherney and Robinson, 1983). Metal analysis (Al, As, B, Ca, Cd, Cr, Cu, K, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti and Zn) was conducted on the samples utilizing an inductively coupled argon plasma emission spectrophotometer (ICAP). Titanium levels were undetectable ( $<.001\mu\text{g ml}^{-1}$ ) in all plant samples (1:70 dilution), indicating that any soil contamination of the plants was insignificant.

## SOIL SAMPLES

Redox potential (Eh) measurements of the soil samples were accomplished by placing five platinum electrodes into each core to a depth of 8 cm. After equilibration overnight, Eh measurements were taken and pH was measured in the exact locations as Eh, utilizing a combination glass-reference electrode.

After the Eh and pH readings were made, subsamples from the top 10 cm of the center of the core were placed in 250 ml polycarbonate centrifuge tubes. The tubes were then capped and the headspace was purged with  $N_2$  gas. The samples were then centrifuged for 20 minutes at 5000 rpm. Soil solutions obtained from this procedure were then filtered under  $N_2$  gas through 0.45  $\mu$ m millipore filters and aliquots were taken for pH, electrical conductivity, titratable alkalinity, titratable acidity, anions, sulfides, total water soluble metals and soluble organic bound metals. Anions ( $Cl^-$  and  $SO_4^{2-}$ ) were analyzed with ion chromatography. Sulfide analyses were conducted with an Orion silver-sulfide selective electrode in sulfide anti-oxidant buffer according to the manufacturers procedure. Soluble organic bound metals were obtained as described by Campbell et al. (1983) except that 10 ml of the soil solution were shaken with 1 gram of Chelex-100 (Na form) cation exchange resin for two hours. After filtering, solutions were acidified to pH 2.0 with nitric acid.

In order to determine exchangeable metals, a 25 g subsample of the centrifuged soil was then placed into preweighed centrifuge tubes containing 100 ml of deaerated 1 N sodium acetate. The pH of the sodium acetate was adjusted to that of each soil by addition of nitric acid.

The centrifuge tubes were then capped and purged with  $N_2$  as described above. After the samples were shaken for two hours, they were centrifuged, filtered, and acidified as described above. Metal analyses were conducted by ICAP.

#### CHEMICAL SPECIATION

The computer program GEOCHEM (Mattigod and Sposito, 1979) was used to speciate metals and calculate ionic strength. The data input consisted of an estimate of ionic strength (based on electrical conductivity), the inorganic concentrations of the water soluble metal fraction (which was defined as the difference between the total water soluble and the soluble organic bound metals),  $SO_4^{2-}$ ,  $Cl^-$ , total carbonate, pH, pe and an estimate of  $pCO_2$  based on pH and bicarbonate concentrations. The ionic strength determined by GEOCHEM was used in conjunction with the Davies equation to determine activity coefficients. Metal activities were then calculated using the free metal output from GEOCHEM and the activity coefficients.

#### EXCHANGEABLE METALS

Exchangeable metals in  $cmoles\ kg^{-1}$  soil were calculated from the sodium acetate extracts using the appropriate dilution factors and correcting for the amount of metals associated with the soil solution remaining after centrifugation for the water soluble fraction.

The amount of metal charge on the CEC attributed to each metal was calculated as follows;

$$q_i = Z_i X_i \quad [1]$$

where  $q_1$  is the metal charge on the CEC accounted for by metal  $i$ ,  $Z_1$  is the valence of metal  $i$ , and  $X_1$  is the amount of metal  $i$  on the CEC in cmoles  $\text{kg}^{-1}$  soil.

The total divalent metal charge on the CEC ( $Q_T$ ) was calculated as the sum of all divalent metal charges on the CEC as follow;

$$Q_T = q_1 + q_2 + q_3 + q_4 \quad [2]$$

where 1, 2, 3 and 4 represent Ca, Fe, Mg, and Mn.

The divalent charge fraction in the exchanger phase (E-Mi) was calculated as described by Sposito et al. (1983) as follows;

$$E-Mi = q_i / Q_T \quad [3]$$

where  $i$  is Ca, Fe, Mg or Mn. Similarly, the divalent charge fraction in the soil solution (E'-Mi) was calculated as follows;

$$E'-Mi = a_i / (a_{Ca} + a_{Fe} + a_{Mg} + a_{Mn}) \quad [4]$$

where  $a_i$  represents the activity of metal  $i$ .

#### GROWTH CHAMBER STUDY

In order to study metal uptake by rice under more controlled conditions, a growth chamber study was conducted utilizing 50 of the acid sulfate soils collected in the field study. After the soils were air dried at room temperature for several months, they were ground by mortal and pestle and sieved (20 mesh). Three hundred and fifty grams of air dried soil were mixed with 0.75 g of ground rice straw and placed in 500 ml plastic containers. Soil water contents were then adjusted to roughly 50% of field capacity. After 30 d of aerobic incubation, the

soils were fertilized with  $75 \text{ mg kg}^{-1}$  N, P, and K (as  $(\text{NH}_4)_2\text{HPO}_4$ , KCl, and urea) and then flooded to a depth of one cm. Duplicate Eh-pH measurements were taken on a weekly basis for the first six weeks of flooding and triweekly for the remainder of the experiment. Twenty one d after flooding, soil subsamples were taken for water soluble and exchangeable metals as described above. After sampling, four seedlings of the R.D. 23 rice variety from Thailand were transplanted into each pot. A second fertilization of N and P (same rates and sources) was made 42 d later by injection into the soil with a hypodermic needle. Daytime temperatures in the growth chamber ranged from 25 to  $35^\circ\text{C}$ , while nighttime temperatures ranged from 20 to  $25^\circ\text{C}$ . At P.D. (112 d after flooding), Eh and pH measurements were made and all aboveground plant parts were removed and dried at  $70^\circ\text{C}$ . Due to inadequate amounts of Y-leaves, the top four leaves of each plant were used for metal analysis. Soil analyses were then made as described above.

## RESULTS AND DISCUSSION

The soil pe and pH measurements taken in the growth chamber and field studies prior to metal sampling are shown in Fig. 1. This figure represents a stability diagram of the Fe minerals considered important in acid sulfate soils (Van Breemen, 1976). These data indicate that many of the pe-pH measurements taken in this study fell in the  $\text{Fe}^{2+}$  field, indicating possible disequilibrium with respect to Fe minerals. A few of the measurements fell in the jarosite and pyrite fields, with the remainder in the siderite and amorphous  $\text{Fe}(\text{OH})_3$  fields.

The average pe-pH values of the 50 soils studied in the growth chamber experiment at different times after flooding is shown in Fig. 2.



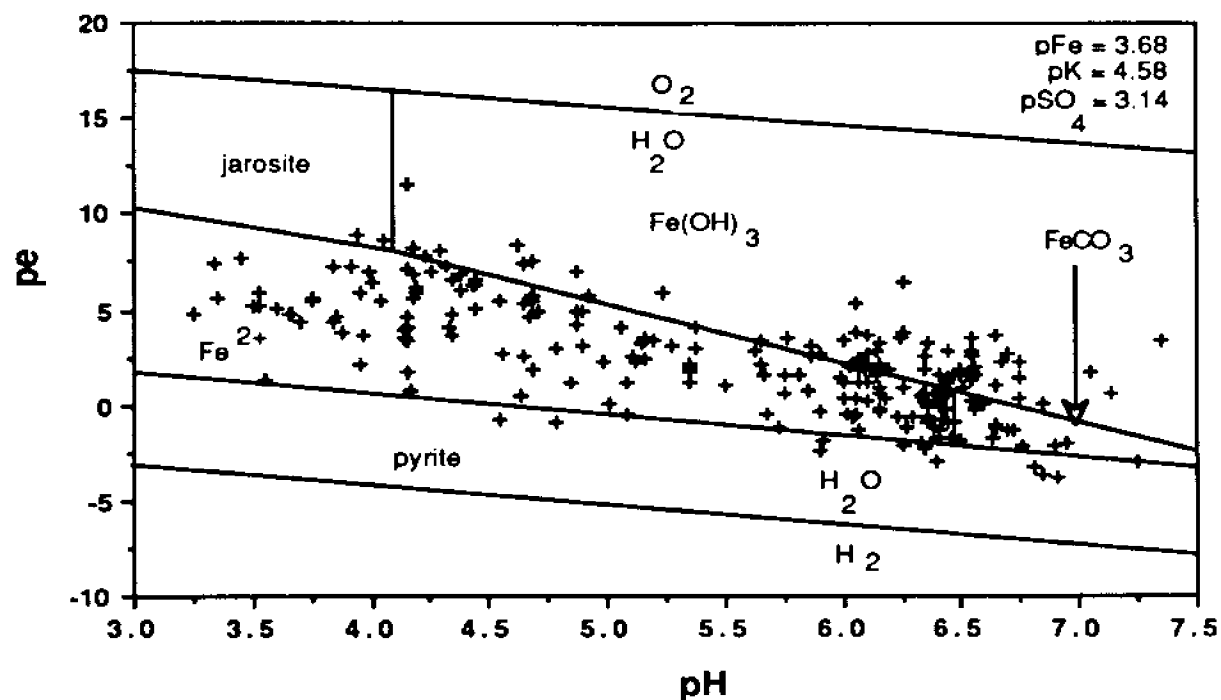


Fig. 1. Stability relations of Fe minerals in acid sulfate soils with pe-pH measurements taken prior to metal sampling in the growth chamber and field studies ( $n = 234$ ).

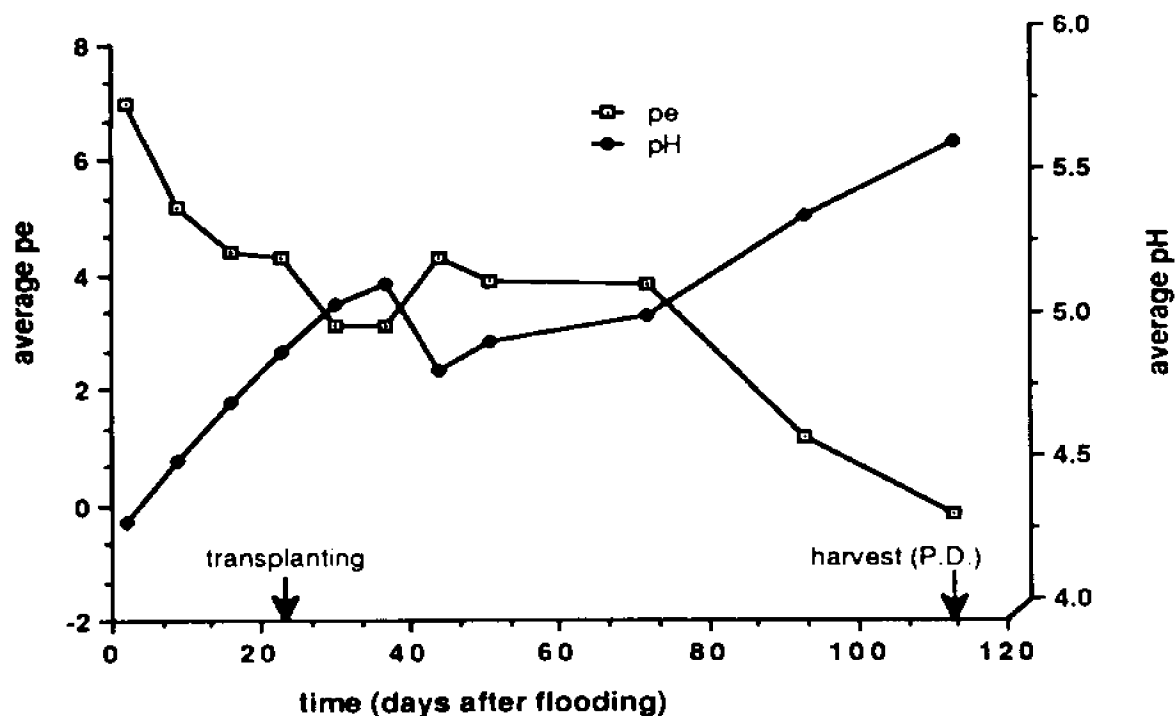


Fig. 2. Average pe and pH measurements of the 50 soils in the growth chamber experiment as a function of time after flooding ( $n = 100$  for each point).

Although average pe and pH values have little or no thermodynamic significance, these data reflect the dynamic nature of the redox chemistry of these soils. This figure indicates that at 112 d after flooding the pH was still increasing and the redox potential was still decreasing. Transient redox conditions such as this are probably normal in most flooded acid sulfate soils since large amounts of acidity must be neutralized before pH's can approach neutrality. These constant fluctuations in the redox environment may result in disequilibrium with respect to Fe minerals.

In Fig. 3  $\log \text{Fe}^{2+}$  activity + 2pH is plotted as a function of pe + pH in a similar manner as that by Schwab and Lindsay (1983). These data indicate that equilibrium between  $\text{Fe}^{2+}$  and pure Fe oxides or hydroxides was the exception rather than the rule in the soils studied. This may be due to the presence of ill-defined ferric oxides as described by Van Breemen (1969) and Langmuir and Whittemore (1971). An alternate explanation of these findings would revolve around the dynamic nature of the redox conditions in these soils as mentioned above. With constantly changing redox conditions, equilibria between  $\text{Fe}^{2+}$  and Fe minerals may be hampered. Another possible explanation of this phenomenon will be discussed later.

Some of the data shown in Fig. 3 suggest that  $\text{FeCO}_3$  may be important in governing  $\text{Fe}^{2+}$  activities in these soils. In order to determine if siderite were a possible stable Fe phase in these soils, the IAP of  $\text{FeCO}_3$  was plotted as a function of pH as shown in Fig. 4. These data indicate that the soils were usually undersaturated with respect to siderite below pH 6.8 and at equilibrium with this phase above this pH. This supports the findings of Schwab and Lindsay (1983)

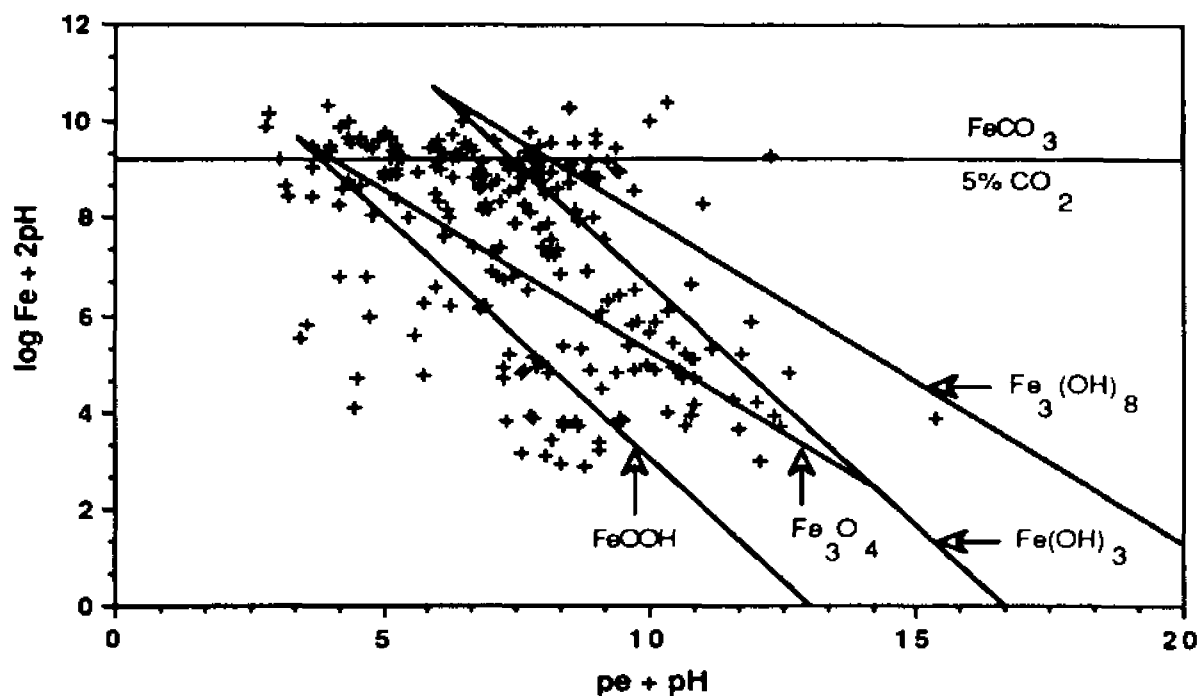


Fig. 3. The relationship between measured  $\text{Fe}^{2+}$  activities and redox conditions in the growth chamber and field studies, with theoretical solubilities for Fe minerals ( $n = 234$ ). Points appearing above or to the right of a line indicate supersaturation, while those below or to the left indicate undersaturation.

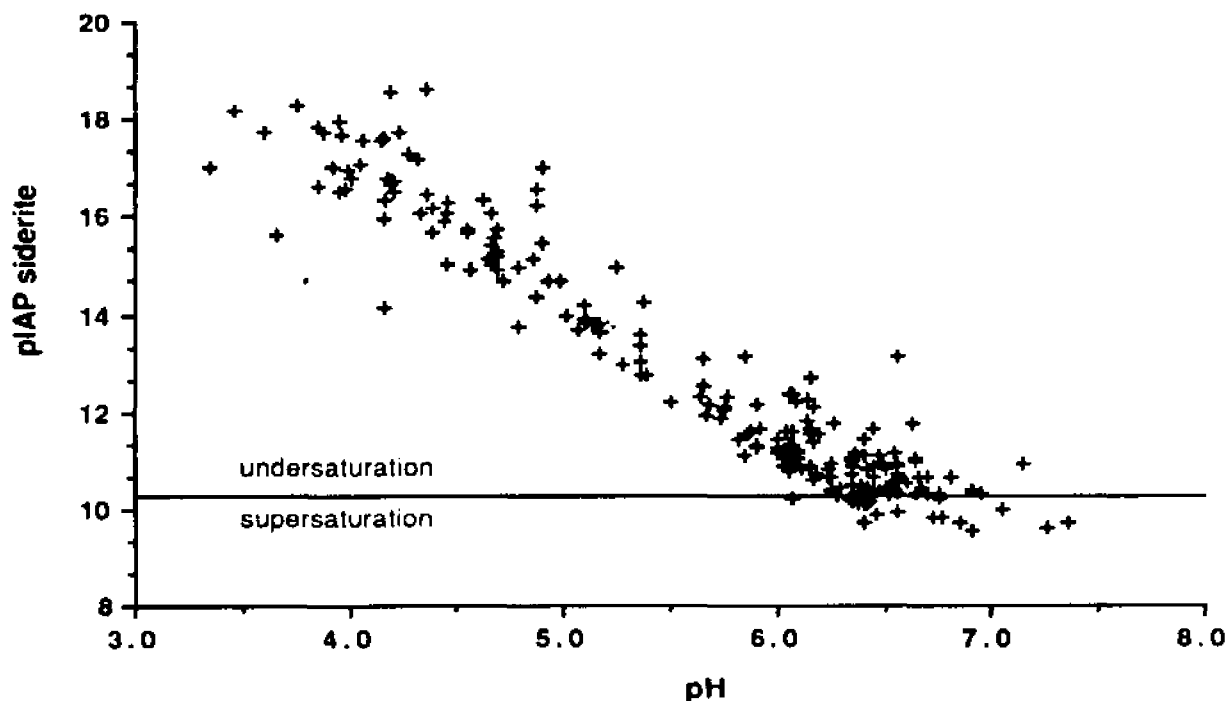


Fig. 4. The negative log of the ion activity product of  $\text{FeCO}_3$  versus pH, from the growth chamber and field studies ( $n = 234$ ).

who demonstrated that  $\text{FeCO}_3$  was important in controlling  $\text{Fe}^{2+}$  in near neutral and alkaline flooded soils.

Another mechanism in which the carbonate chemistry of flooded soils can alter the  $\text{Fe}^{2+}$  activity is through the formation of the ferrous bicarbonate complex ( $\text{FeHCO}_3^+$ ). In order to demonstrate the importance of this mechanism, the  $\text{FeHCO}_3^+/\text{Fe}^{2+}$  concentration ratio in the soil solutions calculated using GEOCHEM were plotted as a function of pH as shown in Fig. 5. These data indicate that  $\text{Fe}^{2+}$  complexing by  $\text{HCO}_3^-$  was considerable in the soils with relatively high pH values.

Although some of the pe-pH measurements made in this study fell in the pyrite field of the theoretical stability diagram shown in Fig. 1 control of  $\text{Fe}^{2+}$  by sulfides could not be evaluated since sulfide concentrations were always below the detection limits of the sulfide electrode used ( $10^{-7}\text{M}$ ). It should be noted that the procedure used employed an anoxic high pH (12.0) buffer solution in conjunction with disodium EDTA and therefore determined free sulfides ( $\text{H}_2\text{S}$ ,  $\text{HS}^-$  and  $\text{S}^{2-}$ ) and not  $\text{S}^{2-}$  per se.

The negative log of  $\text{Fe}^{2+}$  activity ( $\text{pFe}^{2+}$ ) is plotted as a function of exchangeable Fe in Fig. 6. The highly significant correlation shown by these data indicates that a strong relationship exists between  $\text{Fe}^{2+}$  activity and exchangeable Fe. Although this relationship is to be expected, its implications concerning the solubility of  $\text{Fe}^{2+}$ , as well as other metals in flooded acid sulfate soils are far reaching.

Cation exchange is a well known mechanism involved in the control of metal solubilities in soils. However, this mechanism has been ignored as a possible governing force with respect to  $\text{Fe}^{2+}$  solubility in previous studies. The reason for this neglect is understandable

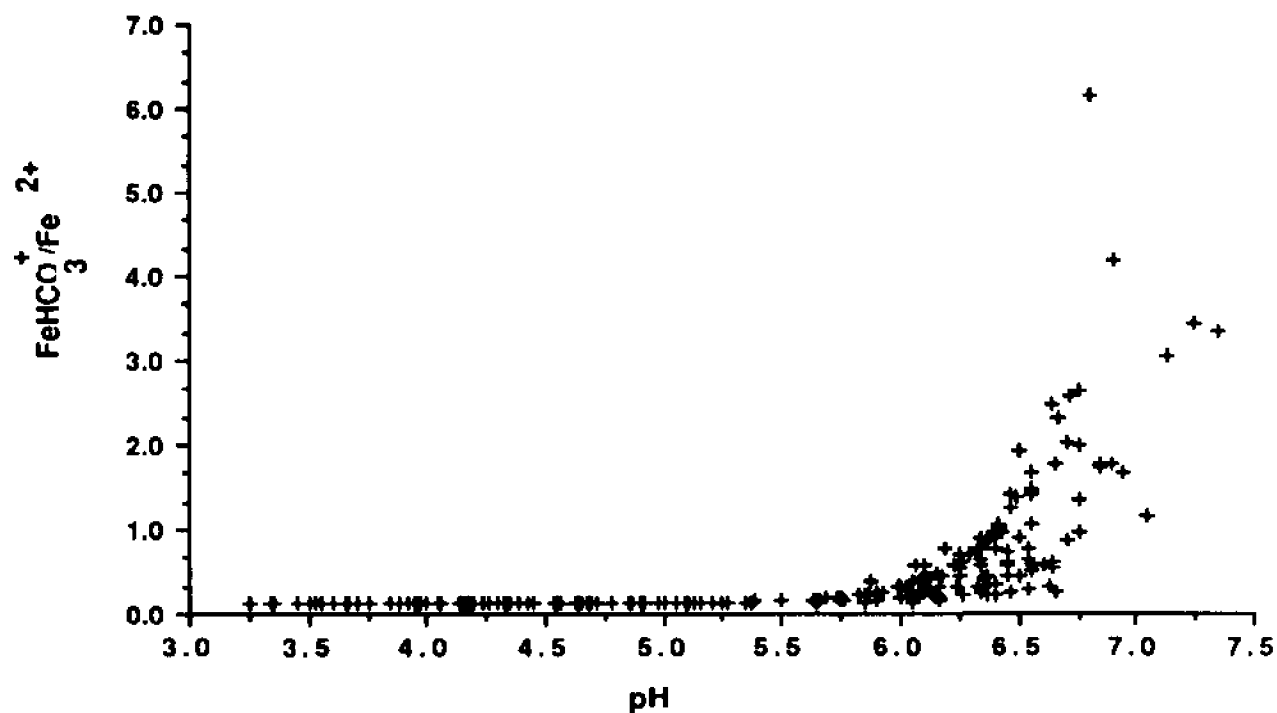


Fig. 5. The concentration ratio of  $\text{FeHCO}_3^+/\text{Fe}^{2+}$  versus pH in the growth chamber and field studies (n = 234).

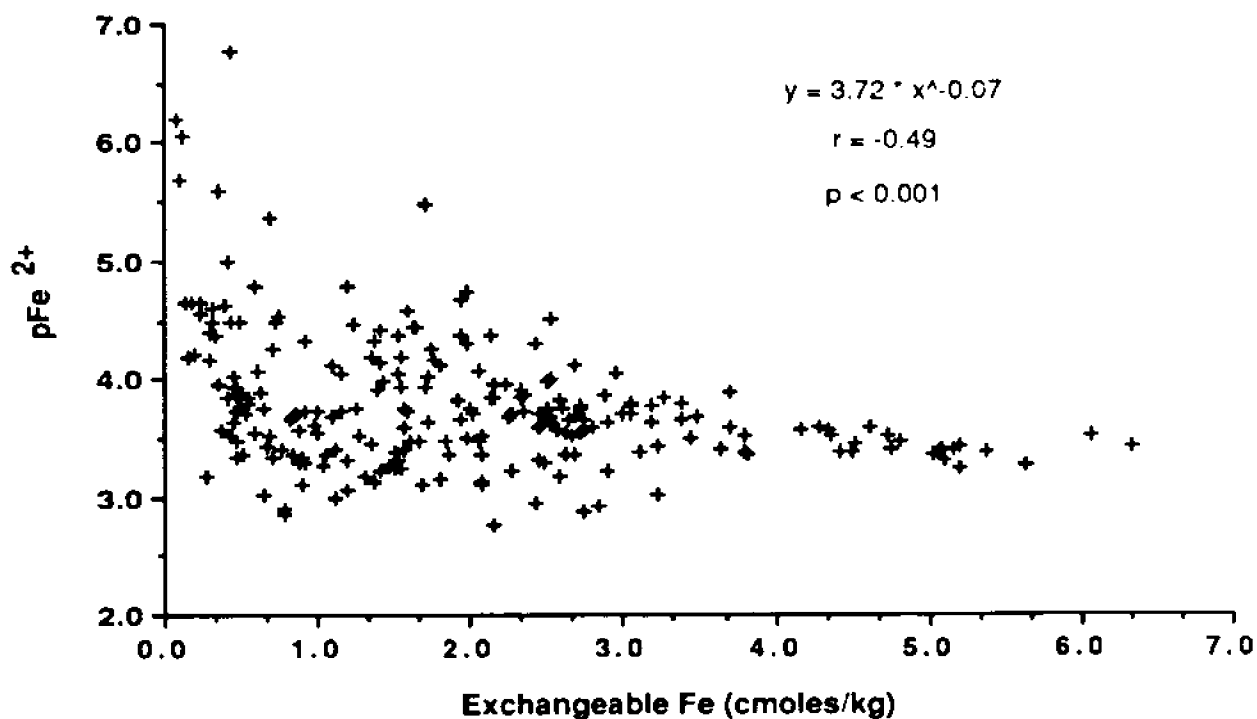


Fig. 6. The relationship between  $\text{Fe}^{2+}$  activity and exchangeable Fe in the growth chamber and field studies (n = 233).

since Fe oxides, hydroxides, sulfides, silicates and carbonates are the predicted stable phases in equilibrium with  $\text{Fe}^{2+}$  under most redox conditions in soils. However, as shown in Fig. 3, equilibrium between  $\text{Fe}^{2+}$  and Fe solid phases in these soils seldom occurred. Two possible explanations of this that were given earlier were the transitory nature of the redox status of these soils and the possible existence of impure or ill-defined ferric oxides. A third mechanism which may be involved is cation exchange.

The divalent charge fraction in the soil solution attributable to  $\text{Fe}^{2+}$  (E'-Fe) is plotted as a function of the divalent charge fraction on the CEC accounted for by Fe (E-Fe) in Fig. 7. The data shown in this figure refer to data believed to be measured without error associated with carbonate complexing, while the samples in which  $\text{FeHCO}_3^+$  compromised more than 1% of the  $\text{Fe}^{2+}$  species as predicted by GEOCHEM were omitted. Since it was not possible to distinguish  $\text{Fe}^{2+}$  from  $\text{FeHCO}_3^+$  on the exchange complex, all exchangeable Fe was assumed to be  $\text{Fe}^{2+}$ , resulting in an overestimation of E-Fe for samples with high concentrations of  $\text{FeHCO}_3^+$ .

The data shown in Fig. 7 indicate that E'-Fe was directly related to E-Fe. The line that makes a 45° angle with both axis refers to the thermodynamic non-preference exchange isotherm (Sposito, 1981). The data shown in this figure suggest that exchange reactions may play an important role in governing the solubility of  $\text{Fe}^{2+}$  in these soils.

Although redox potential and pH are undoubtedly major factors in controlling  $\text{Fe}^{2+}$  solubility, cation exchange also seems to be important. One possible paradigm for  $\text{Fe}^{2+}$  control would involve both precipitation/dissolution reactions as affected by the redox status of

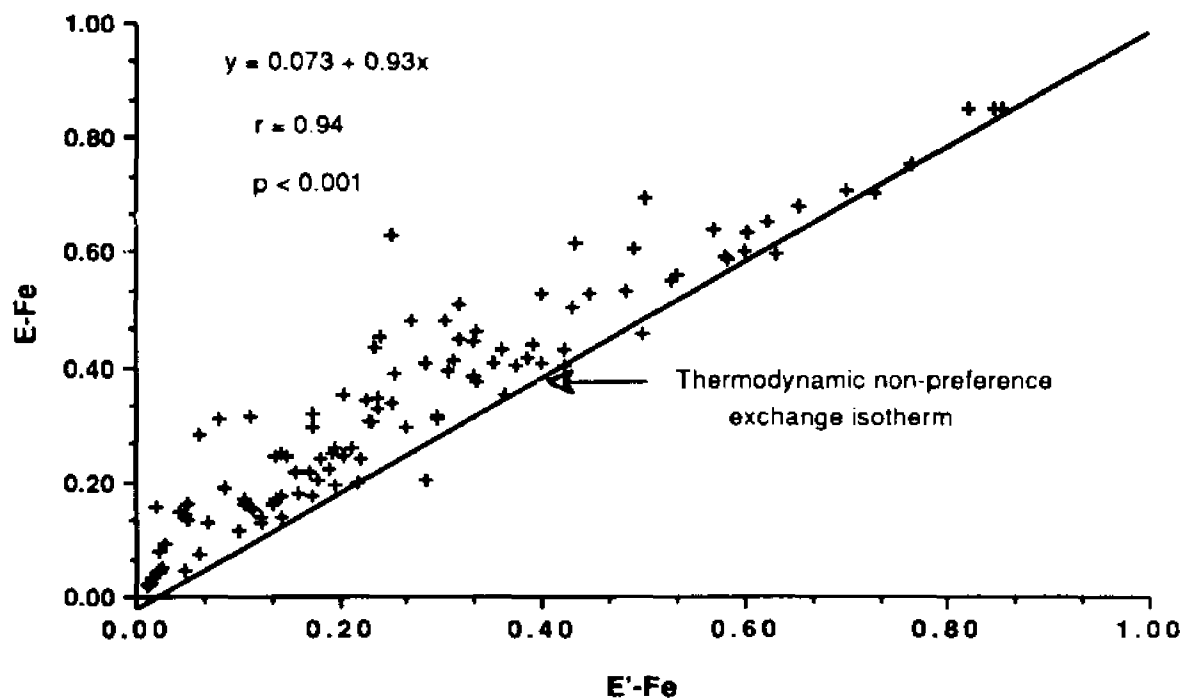


Fig. 7. The relationship between the divalent charge fraction due to Fe on the CEC ( $E\text{-Fe}$ ) and that in solution due  $\text{Fe}^{2+}$  ( $E'\text{-Fe}$ ) in the growth chamber and field studies ( $n = 149$ ).

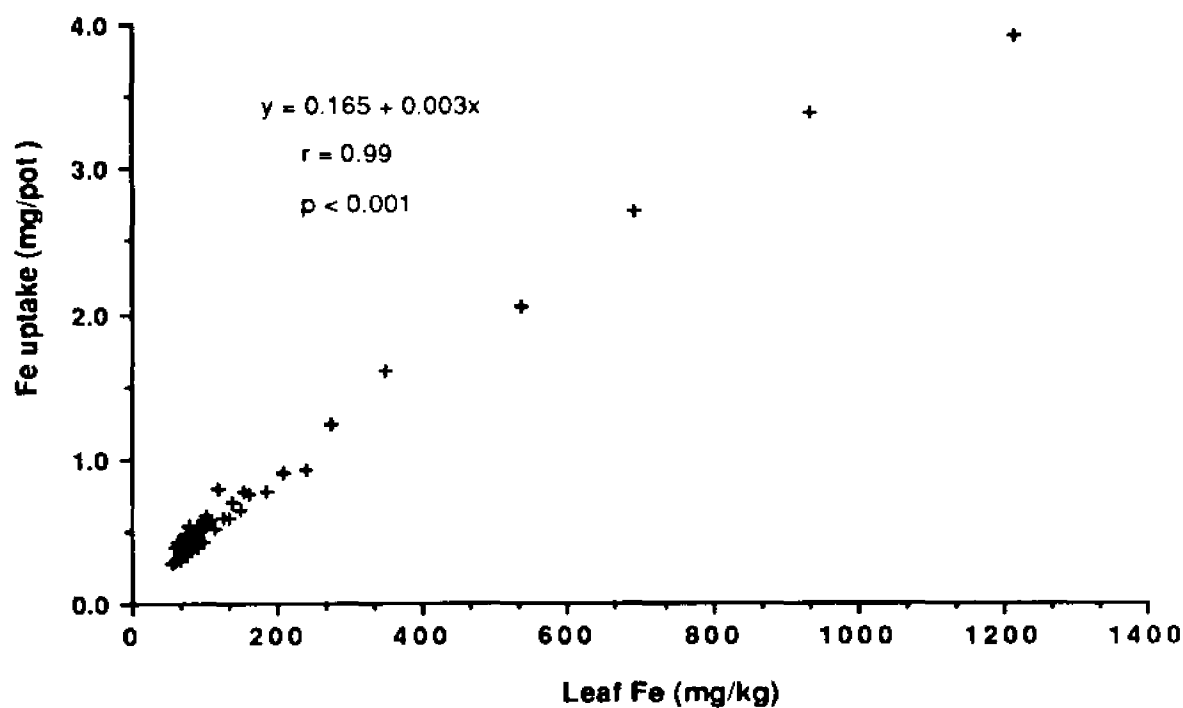


Fig. 8. The relationship between Fe uptake and leaf Fe content in the growth chamber study ( $n = 49$ ).

soils and ion exchange phenomena. In this scenario, ferric oxides or hydroxides would be reduced to  $\text{Fe}^{2+}$  when reducing conditions (lower pe + pH) occurred. As  $\text{Fe}^{2+}$  is released into the soil solution it exchanges with other cations on the CEC. As this process continues, large quantities of Fe build up on the exchange sites. When the redox conditions shift so that a less soluble Fe mineral is the new stable phase, then  $\text{Fe}^{2+}$  would precipitate until the  $\text{Fe}^{2+}$  activity reaches its equilibrium value for the new stable solid phase. However, if the rate of cation exchange exceeds the rate of precipitation, then the  $\text{Fe}^{2+}$  activity would be buffered by exchangeable Fe, causing disequilibrium with respect to the Fe mineral at the specified redox. This phenomenon would occur until the equilibrium  $\text{Fe}^{2+}$  activity was reached and  $E'-\text{Fe}$  equaled  $E-\text{Fe}$ .

The production of  $\text{Fe}^{2+}$  and the accompanying increase in exchangeable Fe will cause  $E'-\text{Fe}$  and  $E-\text{Fe}$  to increase and thus cause  $E'-\text{Ca}$  and  $E-\text{Ca}$  (as well as other divalent cations) to decrease. Since tremendous amounts of  $\text{Fe}^{2+}$  are present in these soils under reducing conditions,  $\text{Fe}^{2+}$  governs the cationic composition of the soil solution in this manner. Although the concentrations of  $\text{Ca}^{2+}$  and other ions in solution may increase as the result of Fe exchange, their availability to plants may actually decrease due to decreases in the mole fraction of these ions.

#### IRON UPTAKE BY RICE

Fe uptake by the plants in the growth chamber study is plotted as a function of leaf Fe content in Fig. 8. The highly positive correlation shown between these parameters indicates that Fe uptake was directly



related to leaf Fe. This figure was included because Fe uptake in the field could not be calculated since dry matter production at P.D. in the field was not evaluated.

Leaf Fe contents of the plants sampled in the growth chamber and field study are plotted as a function of  $pFe^{2+}$  at panicle differentiation in Fig. 9. These data indicate that leaf Fe contents were significantly correlated to  $Fe^{2+}$  activities. These results are consistent with those found by Schwab and Lindsay (1983), Tanaka et al. (1966) and Yoon et al. (1975). Leaf Fe varied from 25 to 1205  $mg\ kg^{-1}$ , with an average of 113  $mg\ kg^{-1}$ . Fe toxicities may have occurred since the reported critical Fe content in rice leaves is 300  $mg\ kg^{-1}$  (Tanaka and Yoshida, 1970). The mean leaf Fe value was comparable to that found by Westfall et al. (1970) in the Y-leaves of healthy rice (98  $mg\ kg^{-1}$ ).

Leaf Fe contents are plotted as a function of  $E'-Fe$  in Fig. 10. These data indicate that leaf Fe contents were more closely related to  $E'-Fe$  than  $Fe^{2+}$  activity alone. The reason for this is probably due to the fact that  $E'-Fe$  takes into account the competition of other ions, whereas  $Fe^{2+}$  activity does not. Similarly,  $E'-Ca$ ,  $E'-Mg$  and  $E'-Mn$  were found to be better predictors of Ca, Mg and Mn uptake, respectively, than their activities (data not shown).

Adams (1966) and Bennett and Adams (1970) showed that the ratio of  $Ca^{2+}$  activity to the sum of the activities of all cations in the soil solution was a better indicator of Ca deficiency than  $Ca^{2+}$  activity alone. They found that treatments which resulted in Ca/total-cation molar activity ratios of less than 0.15 caused growth of shoots and roots to be inhibited. Although they did not report values for Ca uptake, it is probable that the increased growth they measured was

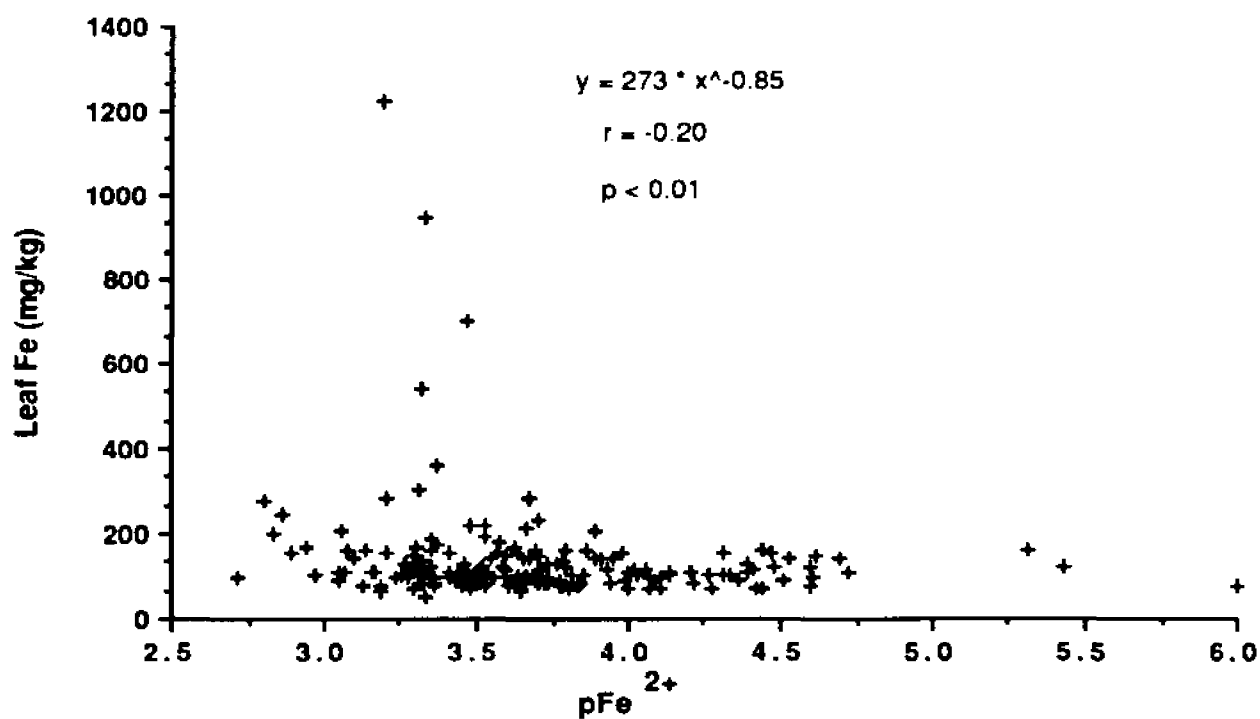


Fig. 9. The relationship between leaf Fe and  $Fe^{2+}$  activity in the growth chamber and field studies (n = 175).

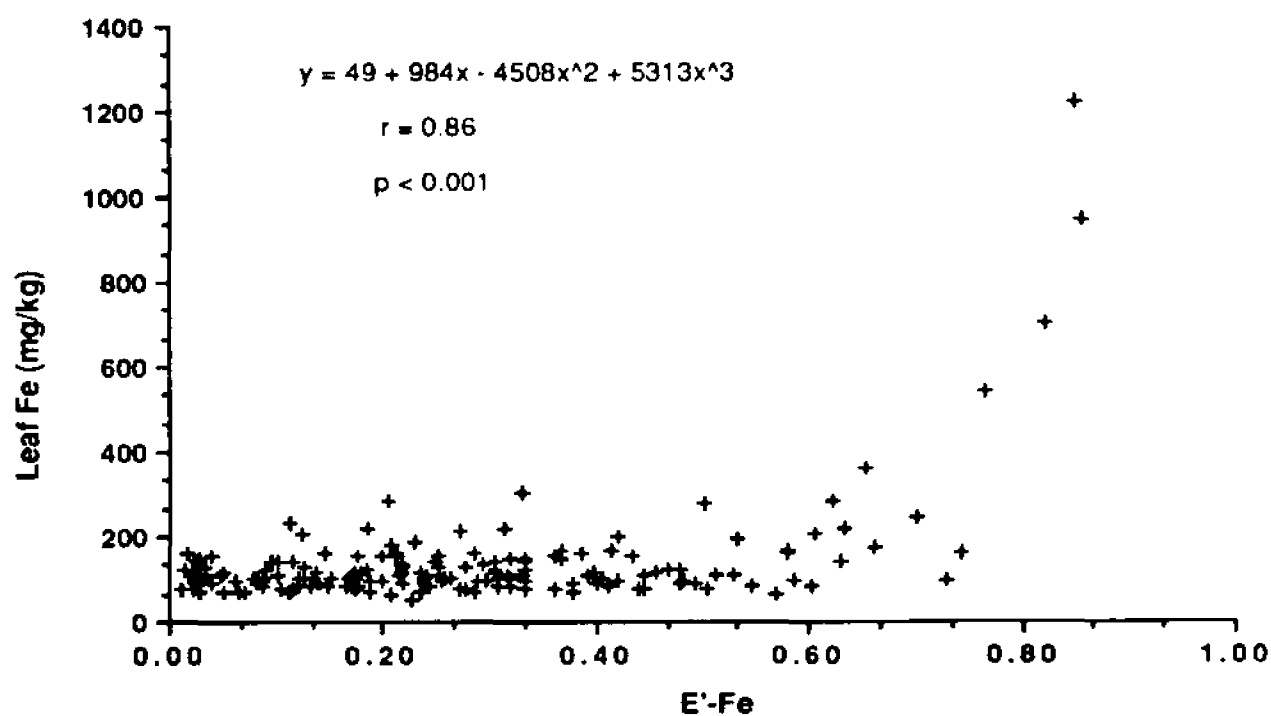


Fig. 10. The relationship between leaf Fe and  $E'-Fe$  in the growth chamber and field studies (n = 175).

indicative of increased Ca uptake. The results of their studies, along with those reported in this investigation, indicate that activity ratios may be more suitable parameters to investigate in plant-soil studies than activity, per se.

These data may also explain why Fe toxicity in rice is often associated with deficiencies in Ca and Mg. Otto et al. (1983), Benckiser et al. (1984b) and Howeler (1973) indicated that Ca and Mg play an important role in Fe toxicity in rice. They stated that a multiple nutritional stress was the main cause of Fe toxicity in rice. Benckiser et al. (1984b) suggested that fertilization with N, P, K, Ca and Mg improved the Fe excluding mechanism of the plant, since root tissues had lower Fe and higher K, Ca and Mg than unfertilized plants. Howeler (1973) reported that the symptoms of Fe toxicity were inversely related to leaf content of P, K, Ca and Mg. Otto et al. (1983) ascribed Fe toxicity to insufficient supplies of K, P, Ca and Mg, rather than to high levels of active iron.

If  $E^+-Fe$  is large, then Fe uptake may occur at the expense of other cations such as Ca and Mg. This hypothesis assumes that divalent cation uptake by rice is somewhat non-specific. Evidence for this was provided by Moore and Patrick (1987) who showed that the uptake of divalent cations (Ca, Cu and Mg) was significantly higher in zinc deficient rice, whereas the uptake of monovalent cations was lower. They suggested that zinc deficient rice concentrates divalent cations at the expense of monovalent cations due to the increased production of a divalent cation carrier.

If the same process were occurring in Ca and/or Mg deficient rice growing in a soil where Fe was the dominant cation in solution, then Fe

uptake would be accelerated and concentrations in the plant would reach toxic proportions. This would also explain why K deficiencies often also occur (ie - divalent uptake at the expense of monovalent).

If  $300 \text{ mg kg}^{-1}$  is indeed the critical Fe content for Fe toxicity in rice, then it would appear from the data shown in Fig. 10 that Fe toxicity in rice can be expected to occur when  $E'-Fe$  exceeds 0.75, and is somewhat independent of the  $Fe^{2+}$  activity.

### CONCLUSIONS

The results presented in this chapter indicated that  $Fe^{2+}$  activities in flooded acid sulfate soils are seldom in equilibrium with pure Fe solid phases under natural conditions. This is believed to be due to (1) transient redox conditions, (2) the presence of ill-defined ferric oxides or hydroxides, and/or (3) cation exchange reactions.

Although leaf Fe contents were significantly correlated to  $Fe^{2+}$  activities, a better relationship existed between leaf Fe and  $E'-Fe$ , indicating that ion competition may be important in determining Fe uptake in rice. The critical  $E'-Fe$  observed for Fe toxicity conditions was approximately 0.75. These findings clarify the role of other nutrients in Fe toxicity in rice.

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### Chapter Three

#### Manganese Availability and Uptake by Rice in Acid Sulfate Soils



## ABSTRACT

Manganese availability and uptake by rice were evaluated in 134 flooded acid sulfate soils in the Central Plains region of Thailand and in a growth chamber experiment utilizing 50 of the same soils. Soil and plant metal analyses were conducted at the panicle differentiation stage of growth in both studies and in the soil prior to transplanting in the growth chamber experiment. Metal activities in soil solutions were determined from free metal concentrations using GEOCHEM and activity coefficients using the Davies equation. Exchangeable metals were determined from sodium acetate extracts buffered to the soil pH.

The results presented in this chapter showed that Mn solid phases such as oxides, hydroxides, carbonates, phosphates or silicates were probably not controlling Mn solubility in these soils. Plots of  $E'-Mn$  versus  $E-Mn$  indicated that cation exchange was probably the dominant mechanism governing  $Mn^{2+}$  activities in these soils.

Manganese uptake in the growth chamber experiment was found to be highly correlated to  $Mn^{2+}$  activity. However, a better relationship was found between Mn uptake and  $E'-Mn$ , indicating that this may be a more suitable availability index than activity alone. Manganese uptake was also found to be highly correlated to  $p(Mn^{2+}/Fe^{2+})$ , indicating that the Fe:Mn interaction may be more specific than the interaction between Mn and other cations. Patterns of Mn uptake under field conditions were similar to that found in the growth chamber study.

Key words - Cation exchange, flooded soils,  $Mn^{2+}$  activity, mineral equilibria, GEOCHEM.

Physico-chemical parameters such as pH and Eh profoundly effect the solubility of Mn in soils. Under anoxic and/or acidic conditions, Mn(IV) and Mn(III) oxides and hydroxides are reduced to the more soluble manganous form. Adams and Wear (1957) stated that Mn solubility in aerated soils is extremely pH dependant, with appreciable amounts being brought into solution below pH 5.0. Patrick and Turner (1968) noted that an increase in water soluble and exchangeable Mn was one of the first measurable effects of reducing conditions brought on by waterlogging. They found that the easily reducible Mn fraction decreased by approximately 80% in less than 40 days. Mandal and Mitra (1982) showed increases in water soluble plus exchangeable Mn at the expense of the reducible fraction following flooding. Gotoh and Patrick (1972) found that below pH 5.0 almost all the reducible Mn was converted to water soluble and exchangeable Mn. However, equilibria calculations showed that the observed  $pMn/pH$  slope and  $E^0$  they found were much lower under high pH conditions than the theoretical values. They concluded that cation exchange reactions were important in regulating water soluble Mn.

Several other researchers have attempted to explain Mn solubility in natural waters assuming various solid phases control Mn availability. Bohn (1970) found that  $Mn^{2+}$  concentrations predicted from Eh and pH measurements assuming pyrolusite control were quite different from observed values. Likewise, Collins and Buol (1970) were unable to relate Eh, pH and  $Mn^{2+}$  concentrations with theoretical values. Studies of this nature conducted on near neutral to alkaline soils have usually been more successful in predicting solid phases controlling Mn

solubility. Ponnampetuma et al. (1969) found that reduced  $\text{Mn}^{2+}$  can precipitate as rhodocrosite ( $\text{MnCO}_3$ ) or as oxides or hydroxides of  $\text{Mn}^{2+}$  under non-acid conditions. Pasricha and Ponnampetuma (1976) also showed that  $\text{MnCO}_3$  may have controlled  $\text{Mn}^{2+}$  levels in flooded rice soils. Schwab and Lindsay (1983) demonstrated that under alkaline conditions rhodocrosite was implicated in controlling Mn solubility if the  $\text{pe} + \text{pH}$  was below 16. However, they were unable to explain Mn solubility in terms of any solid phase when the soil pH was below 7.0.

Later work by Boyle and Lindsay (1986) showed that manganese phosphates may control Mn solubility in some soils. Using theoretical stability diagrams they concluded that  $\text{MnPO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Mn}_5\text{H}_2(\text{PO}_4)_4 \cdot \text{H}_2\text{O}$  were the most stable Mn solid phases if strengite-soil Fe or variscite-gibbsite equilibria were controlling P. They also found that under alkaline conditions a number of soils were slightly saturated with respect to  $\text{MnPO}_4 \cdot 1.5\text{H}_2\text{O}$ , and with time supersaturation decreased causing the IAP's to approach the solubility product ( $K^0$ ).

Van Breeman (1976) noted that the Eh-pH range in many flooded acid sulfate soils from Thailand fell in the  $\text{Mn}^{2+}$  field of theoretically constructed Eh-pH stability diagrams of the  $\text{Mn-H}_2\text{O-CO}_2$  system. He concluded that Mn was present mainly in the water soluble and exchangeable form in these soils.

Studies conducted on Mn availability to rice have often been contradictory. Clark et al. (1957) and Chaundry and McLean (1963) found that flooding a soil greatly increased Mn uptake by rice. In a laboratory study, Jugsuwinda and Patrick (1977) found greater Mn uptake by rice grown under reducing conditions than oxidizing. In contrast, Sinewirante and Mikkelsen (1961) showed that Mn uptake decreased upon

flooding, while Patrick and Fontenot (1976) found that flooding had little or no effect on Mn uptake by rice. Studies in which solution Mn was measured have shown increases in uptake with increasing Mn concentrations or activities (Schwab and Lindsay, 1983, Tanaka and Navasero, 1966a; Yoon et al., 1975).

Several workers have indicated a strong interaction exists between Fe and Mn uptake in rice. Tanaka and Navasero (1966b) conducted hydroponic experiments to determine the relationship between Fe and Mn uptake in rice. They found that increases in the Fe level in the growth media caused decreases in the Mn contents of the plants and vice versa. Vlamis and Williams (1964) also showed decreases in Fe contents as Mn in hydroponic solution was increased. Similarly, Nhung and Ponnampetuma (1966) showed that  $MnO_2$  applications to acid sulfate soils caused decreased Fe uptake. In contrast, Swarup (1981) showed Fe applications to sodic soils increased Mn availability to rice. However, he stated that this effect may have been due to the acidifying potential of the  $FeSO_4$  used since the soil pH decreased from 9.4 to 9.1 after fertilization. Van Der Vorm and Van Diest (1979) stated that the absorption of Mn by rice is little effected by large quantities of Fe.

The objectives of this study were; (1) to measure the solubility of Mn in flooded acid sulfate soils cropped to rice, (2) to determine what controls Mn solubility in these soils and (3) to determine the relationships between soil parameters and Mn uptake by rice.

#### METHODS AND MATERIALS

A description of the methods and materials for the two studies discussed in this chapter is given in chapter two.

## RESULTS AND DISCUSSION

In Fig. 1,  $\log \text{Mn}^{2+} + 2\text{pH}$  is plotted as a function of  $\text{pe} + \text{pH}$  in a manner similar to that of Schwab and Lindsay (1983). The points that appear below or to the left of the lines indicate undersaturation with respect to these phases. These data indicate that oxides and hydroxides of Mn are probably not controlling its solubility, since  $\text{Mn}^{2+}$  activities were much lower than would be predicted by these phases. This supports the findings of Van Breeman (1976) who showed that in most acid sulfate soils the Eh-pH values corresponded to the  $\text{Mn}^{2+}$  field of theoretically constructed Eh-pH stability diagram of the  $\text{Mn-H}_2\text{O-CO}_2$  system.

The negative log of the ion activity product (pIAP) of rhodochrosite is plotted as a function of pH in Fig. 2. These data indicate that under acid conditions the soils were undersaturated with respect to rhodochrosite, implying that this solid phase should not be responsible for the measured solubilities of  $\text{Mn}^{2+}$  observed under these conditions. However, the two soils with the highest pH values appeared to be in equilibrium with rhodochrosite. These data confirm that under basic conditions, rhodochrosite may form in flooded soils as predicted by Pasrica and Ponnampetuma (1976), Ponnampetuma et al. (1969) and Schwab and Lindsay (1983).

The maximum IAP's and equilibrium constants for several other Mn minerals are shown in Table 1. These data indicate that phosphate and silicate minerals probably did not play an active role in governing Mn solubility in these soils. Control of Mn by sulfides could not be evaluated since free sulfide concentrations were below the detection limit of the selective ion electrode used ( $10^{-7}$  M).

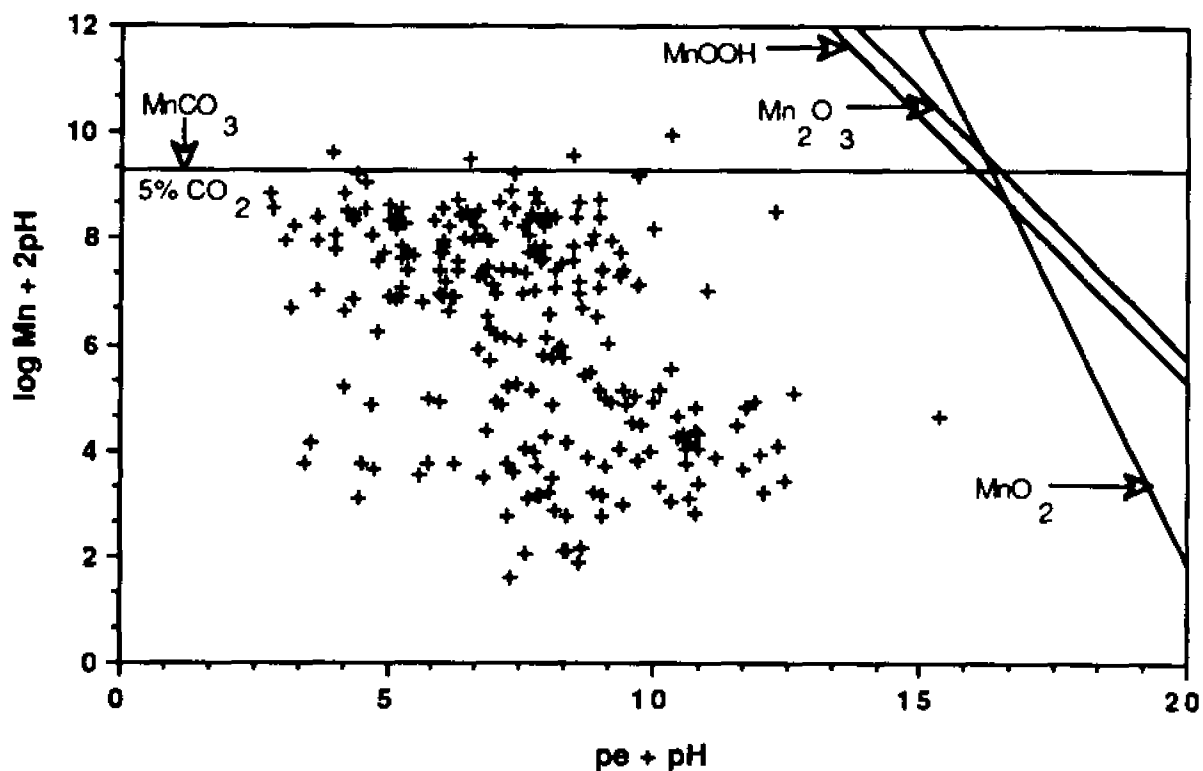


Fig. 1. The relationship between  $\text{Mn}^{2+}$  activities and redox conditions in the growth chamber and field studies, with theoretical solubilities of Mn minerals ( $n = 234$ ).

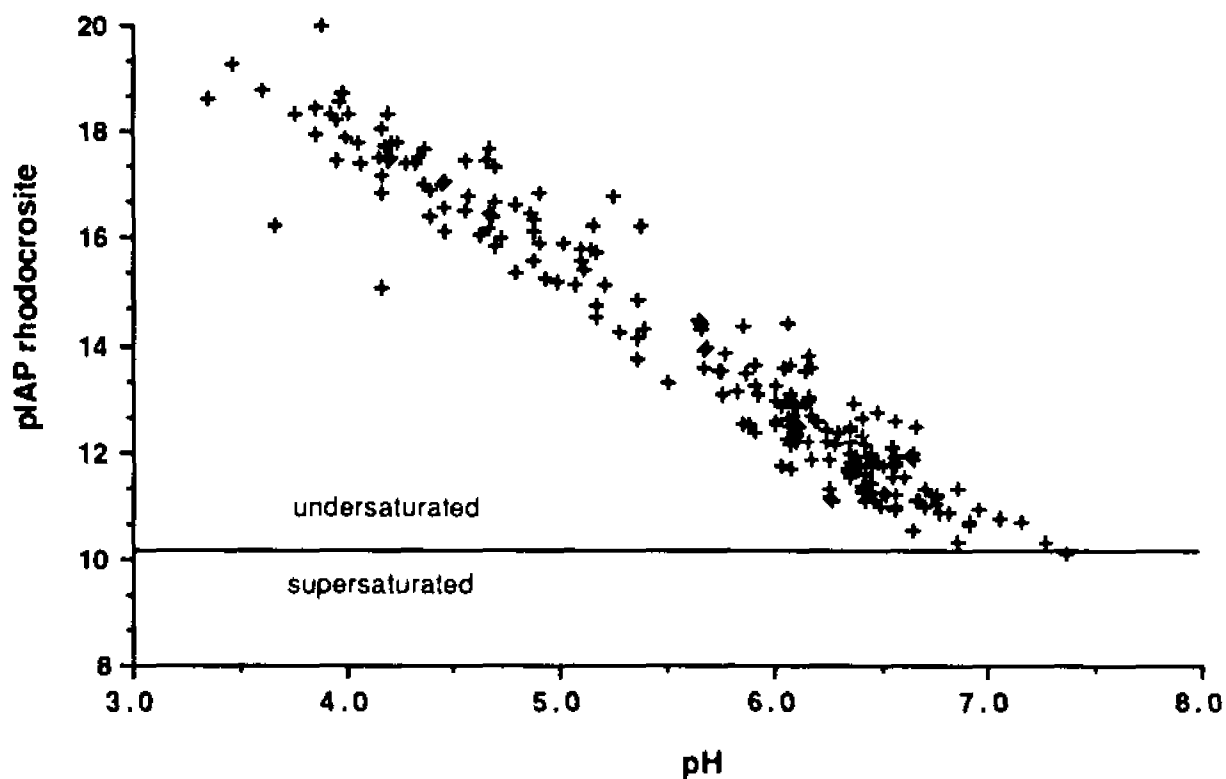


Fig. 2. The relationship between  $\text{pIAP}$  of  $\text{MnCO}_3$  and  $\text{pH}$  from the growth chamber and field studies ( $n = 234$ ).

Table 1 - Ion activity products and equilibrium constants of selected Mn minerals.

Reaction	pIAPmax*	pK	reference
$\text{Mn}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O} = 5\text{Mn}^{2+} + 2\text{H}^+ + 4\text{PO}_4^{3-} + 4\text{H}_2\text{O}$	75.1	73.4	1
$\text{Mn}_3(\text{PO}_4)_2 = 3\text{Mn}^{2+} + 2\text{PO}_4^{3-}$	33.1	27.3	1
$\text{MnPO}_4 \cdot 1.5\text{H}_2\text{O} = \text{Mn}^{3+} + \text{PO}_4^{3-} + 3/2\text{H}_2\text{O}$	35.3	34.2	1
$\text{MnHPO}_4 \cdot 3\text{H}_2\text{O} = \text{Mn}^{2+} + \text{PO}_4^{3-} + \text{H}^+ + 3\text{H}_2\text{O}$	21.0	19.8	1
$\text{MnSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Mn}^{2+} + \text{H}_4\text{SiO}_4^0$	-1.19	-10.3	2

\* - negative log of ion activity product (maximum observed)

1 - Boyle and Lindsay (1986)

2 - Lindsay (1979)

If Mn solid phases are not regulating levels of  $Mn^{2+}$  in solution, the only other possible mechanism of control is through cation exchange reactions. In order to determine if exchange reactions were important in governing the solubility of  $Mn^{2+}$ ,  $E'-Mn$  was plotted as a function of  $E-Mn$  as shown in Fig. 3.  $E'-Mn$  is the divalent cation charge fraction in the soil solution attributable to Mn (ie -  $Mn^{2+}/Mn^{2+}+Fe^{2+}+Ca^{2+}+Mg^{2+}$ ) and  $E-Mn$  is the divalent charge fraction on the CEC attributable to Mn. The solid line in this figure represents the thermodynamic non-preference exchange isotherm. These data provide strong evidence that  $Mn^{2+}$  activities in flooded acid sulfate soils are regulated by cation exchange reactions. Van Breeman (1976) stated that Mn was mainly in the dissolved and exchangeable form in flooded acid sulfate soils. Gotoh and Patrick (1977) also suggested that exchange reactions play an important role in regulating water soluble Mn in flooded soils.

Although there is some deviation from the thermodynamic non-preference isotherm in Fig. 3, the relationship between  $E'-Mn$  and  $E-Mn$  is close to what would be predicted if non-preferential cation exchange were controlling  $Mn^{2+}$  activities in these soils. Classical exchange isotherms developed from one soil or a pure clay in a non-complexing medium such as a perchlorate background would undoubtedly conform better to the non-preference line.

#### MANGANESE UPTAKE BY RICE - GROWTH CHAMBER STUDY

Manganese uptake by the plants in the growth chamber experiment is plotted as a function of  $pMn^{2+}$  at panicle differentiation in Fig. 4. These data show that Mn uptake by the plants was significantly



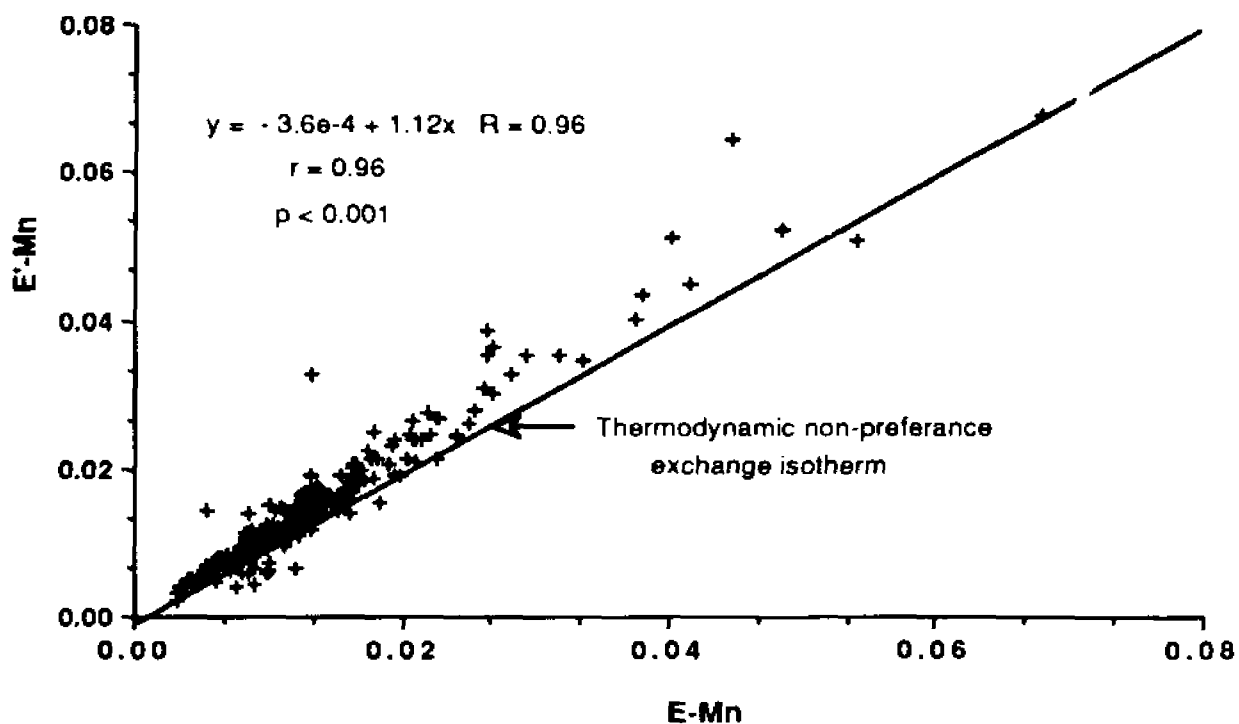


Fig. 3. The relationship between  $E'-Mn$  and  $E-Mn$  in the growth chamber and field studies ( $n = 233$ ).

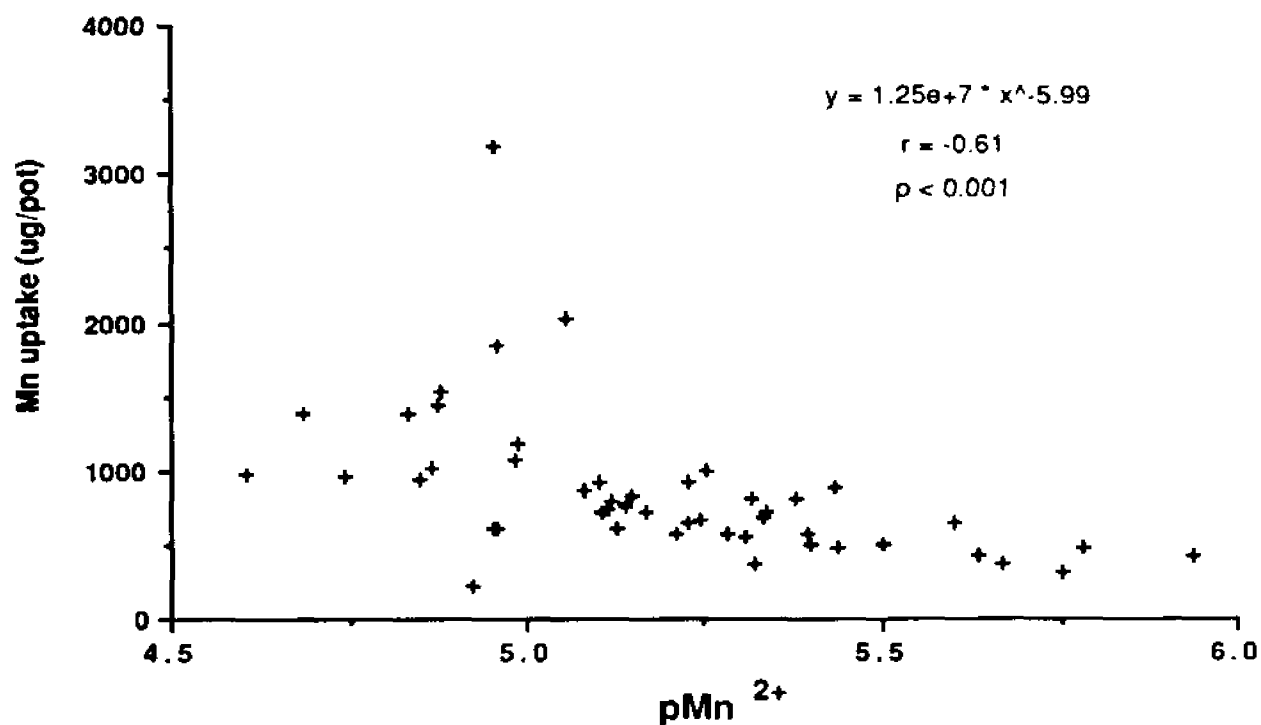


Fig. 4. The relationship between Mn uptake and  $Mn^{2+}$  activity in the growth chamber study ( $n = 49$ ).

correlated with  $Mn^{2+}$  activity. These results are consistent with those found by Schwab and Lindsay (1983) who also showed Mn uptake to be related to  $Mn^{2+}$  activity. Other workers have shown that Mn uptake by rice was correlated with Mn in solution (Tanaka and Navasero, 1966a; Yoon et al., 1975).

Manganese uptake is plotted as a function of  $E'-Mn$  in Fig. 5. These data indicate that Mn uptake was more closely related to the divalent charge fraction in the soil solution accounted for by Mn than  $Mn^{2+}$  activity alone. Therefore,  $E'-Mn$  is probably a better indicator of Mn availability to rice than  $Mn^{2+}$  activity. Iron uptake was also shown to be more closely related to  $E'-Fe$  than  $Fe^{2+}$  activity (chapter two). Similarly, the ratio of  $Ca^{2+}$  activity to the sum of the activities of all cations in the soil solution has been shown to be a better indicator of Ca deficiency in cotton and sudangrass than  $Ca^{2+}$  activity (Adams, 1966; Bennett and Adams, 1970; Howard and Adams, 1965). The results of this study and those found by Adams and his co-workers demonstrate that under many circumstances activity ratios may be more suitable parameters to investigate than activities when studying nutrient uptake. This is probably due to the fact that activity ratios reflect ion competition for nutrient uptake sites of the plant. If competitive inhibition for uptake sites is occurring, then it is logical to include competing ions in availability indices.

The highest Mn uptake in the growth chamber experiment was shown to occur at an intermediate level of  $E'-Mn$  (Fig. 5). Although this rather anomalous point would appear to contradict the hypothesis that metal uptake is influenced by ion interaction, it in fact illuminates a more specific interaction; that of Fe and Mn. Manganese uptake is plotted as

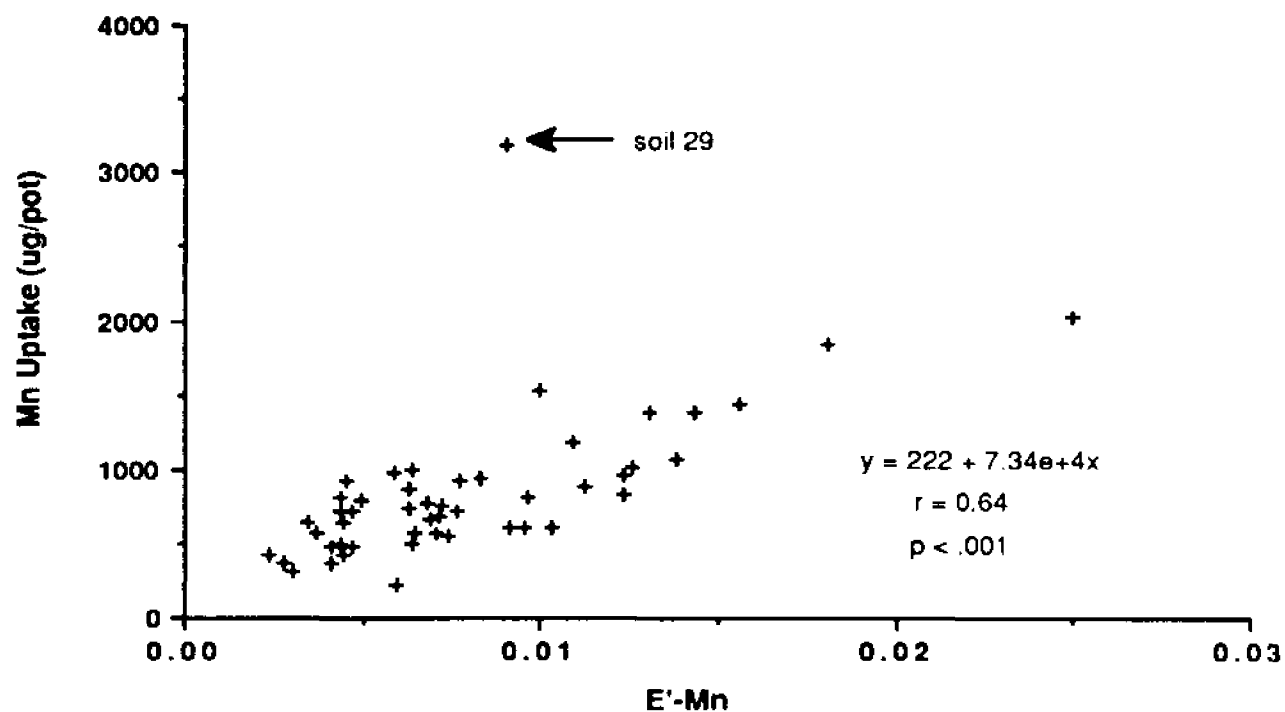


Fig. 5. The relationship between Mn uptake and E'-Mn in the growth chamber study (n = 49).

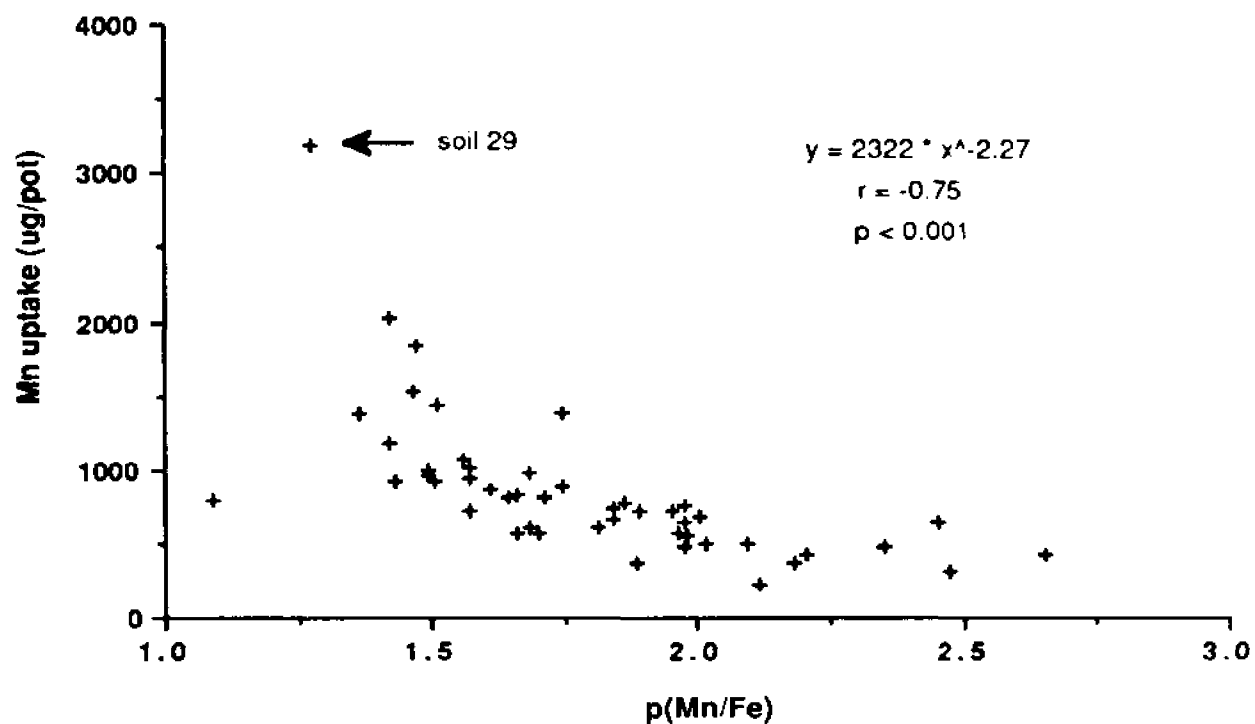


Fig. 6. The relationship between Mn uptake and the ratio of Mn/Fe activities in the growth chamber study (n = 49).

a function of the  $Mn^{2+}/Fe^{2+}$  activity ratio in Fig. 6. This figure shows that the highest Mn uptake occurred when the  $Mn^{2+}/Fe^{2+}$  activity ratio was very high, suggesting that Fe is antagonistic to Mn uptake in rice. The strong interaction shown between these ions may be due to similar physico-chemical characteristics, such as the ability to undergo oxidation-reduction reactions.

Iron-manganese interactions in rice have been the subject of several studies. Nhung and Ponnampetrum (1966) showed that  $MnO_2$  additions to acid sulfate soils resulted in a decrease in Fe toxicity in rice. Tanaka and Navarero (1966b) reported high Fe levels in nutrient solutions resulted in decreased Mn uptake by rice, which is consistent with the findings of this study. However, Van Der Dorm and Van Diest (1979) concluded that low Mn uptake by rice was due to low Mn concentrations in the soil and not necessarily to high Fe levels. Although these findings appear contradictory to the above discussion, it may be that reduced Mn levels caused lower Mn/Fe ratios in the soils they studied, which would also result in Fe antagonism.

Manganese uptake is plotted as a function of leaf Mn content in Fig. 7. The highly positive correlation shown between these parameters indicates that Mn uptake was directly related to leaf Mn. This figure was included because Mn uptake in the field could not be calculated since dry matter production at panicle differentiation in the field was not evaluated.

#### FIELD STUDY

Leaf Mn contents from the plants sampled in the field study are plotted as a function of  $pMn^{2+}$  in Figure 8. These data indicate that Mn

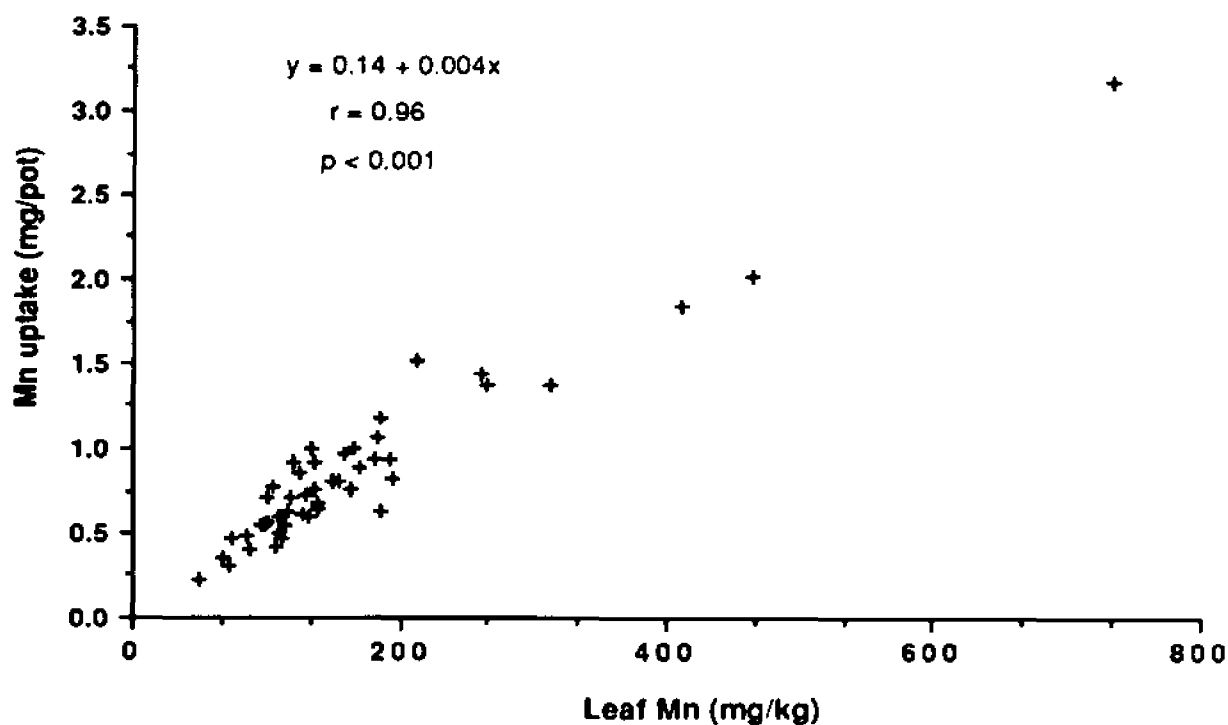


Fig. 7. The relationship between Mn uptake and leaf Mn in the growth chamber study (n = 49).

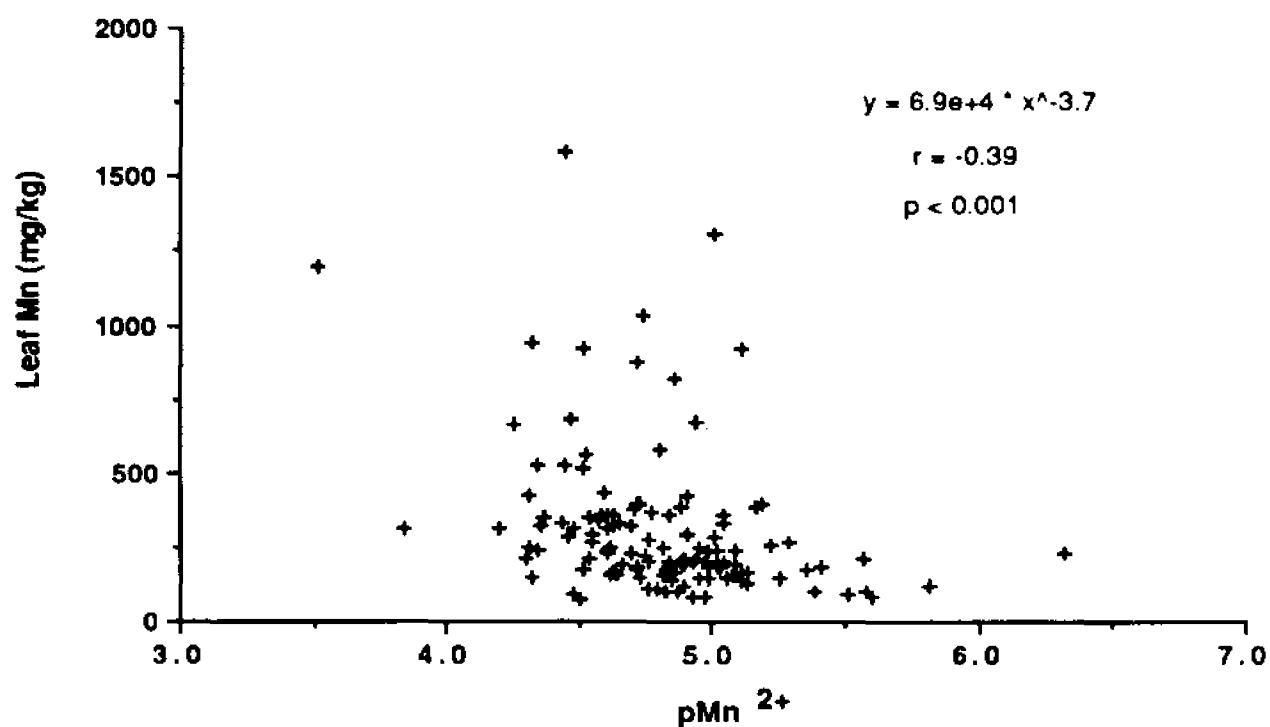


Fig. 8. The relationship between leaf Mn and  $Mn^{2+}$  activity in the field study (n = 126).

uptake increased with increases in  $\text{Mn}^{2+}$  activity, as was found in the growth chamber study. Leaf Mn varied from 34 to 1551  $\text{mg kg}^{-1}$ , with an average of 275  $\text{mg kg}^{-1}$ . Since the critical Mn level in rice for toxicity to occur has been suggested to be 6000  $\text{mg kg}^{-1}$ , Mn toxicity was not suspected. The average leaf Mn content found in this study was somewhat lower than that found by Yoon et al. (1975) in the Y-leaves of rice grown in Arkansas (810  $\text{mg kg}^{-1}$ ).

Leaf Mn contents observed in the field are plotted as a function of  $E'-\text{Mn}$  in Figure 9 and the  $\text{Mn}^{2+}/\text{Fe}^{2+}$  activity ratio in Figure 10. Although there is quite a bit of scatter in these data, these figures indicate that Mn uptake was probably influenced by the ratio of the activities of these ions in solution, as was found in the growth chamber experiment.

The average leaf Fe content observed under field conditions was 113  $\text{mg/kg}$  (Moore and Patrick, 1987), which is much lower than the average leaf Mn contents reported above. Since  $\text{Fe}^{2+}$  activities were on the average an order of magnitude higher than  $\text{Mn}^{2+}$  activities ( $10^{-4}$  versus  $10^{-5}$ ), Fe precipitation at the root surface was considered to be greater than that of Mn. This is supported by the fact that reduced Fe is oxidized at a lower redox potential than reduced Mn (Patrick and Reddy, 1978).

## CONCLUSIONS

The results reported in this chapter showed that flooded acid sulfate soils are generally undersaturated with respect to most Mn solid phases. Plots of  $E'-\text{Mn}$  versus  $E-\text{Mn}$  indicate that exchange reactions are probably controlling solution  $\text{Mn}^{2+}$  in these soils. Manganese uptake by

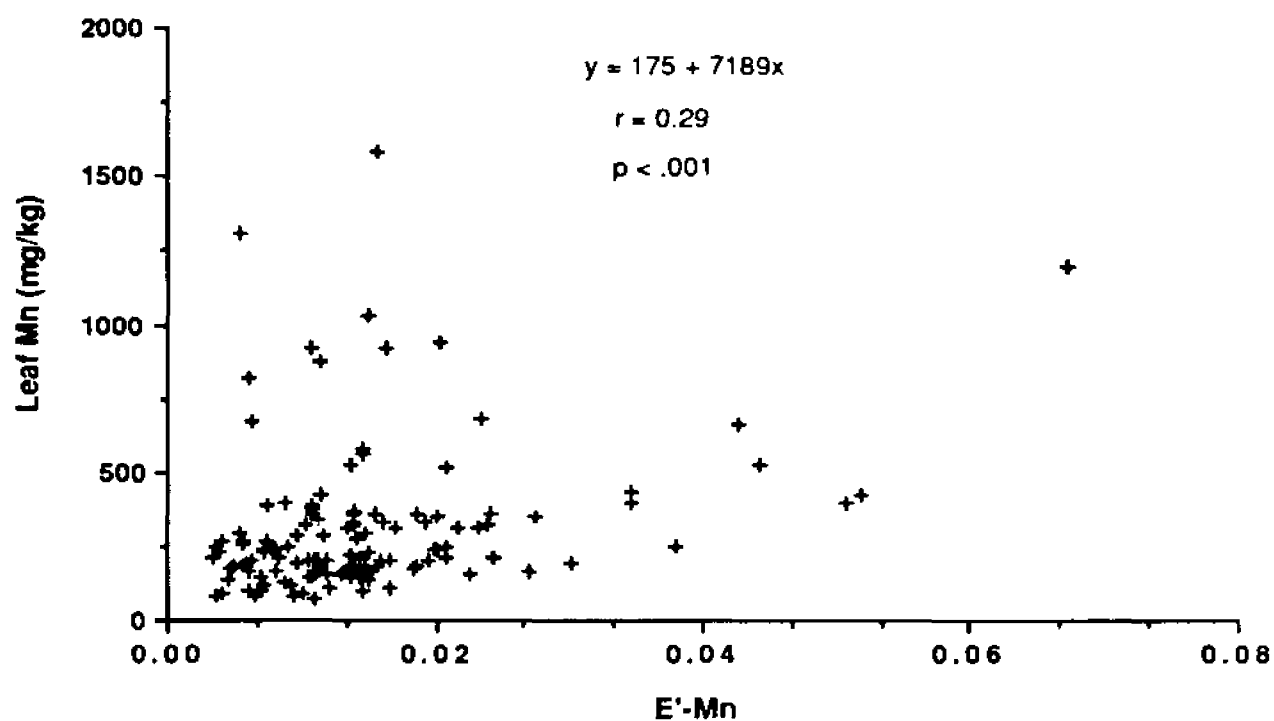


Fig. 9. The relationship between leaf Mn and  $E'-Mn$  in the field study ( $n = 126$ ).

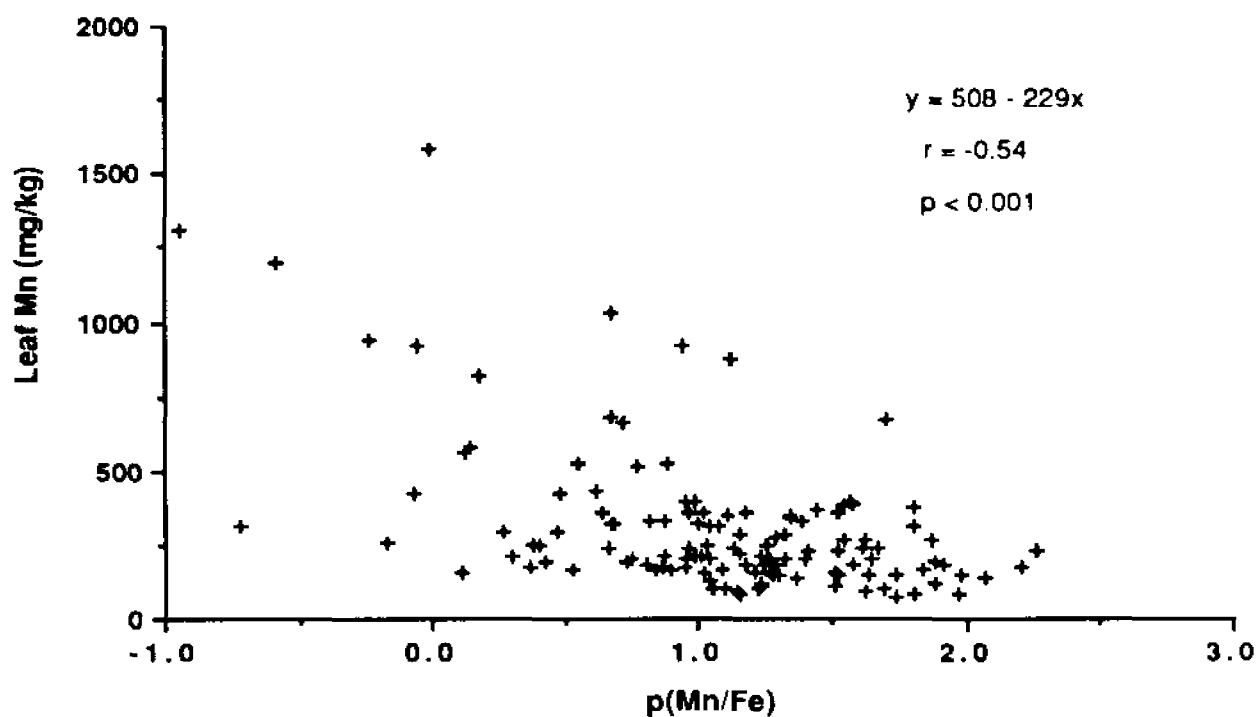


Fig. 10. The relationship between leaf Mn and the ratio of Mn/Fe activities in the field study ( $n = 126$ ).

rice was more closely related to  $E'-Mn$  than to  $Mn^{2+}$  activity in the growth chamber study, possibly due to ion interactions. Manganese uptake was also shown to decrease as the  $Mn/Fe$  activity ratio decreased.



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## Chapter Four

### Calcium and Magnesium Availability and Uptake by Rice in Acid Sulfate Soils

## ABSTRACT

Calcium and Mg availability and uptake by rice were evaluated in 134 flooded acid sulfate soils in the Central Plains region of Thailand and in a growth chamber study utilizing 50 of the same soils. Soil and plant metal analyses were conducted at the panicle differentiation stage of growth in both studies and in the soil prior to planting in the growth chamber experiment. The R.D. 23 rice variety was used in the growth chamber study, while 88 different varieties were sampled in the field study. Metal activities were determined from free metal concentrations using GEOCHEM and activity coefficients using the Davies equation. Exchangeable metals were determined from sodium acetate extracts buffered to the soil pH.

The results of this study indicate that the soils studied were generally undersaturated with respect to most Ca and Mg minerals. Exchange isotherms indicated that cation exchange reactions probably govern the solubility of  $\text{Ca}^{2+}$  and to a large degree  $\text{Mg}^{2+}$  in acid sulfate soils. However, Mg-bearing minerals may also contribute to  $\text{Mg}^{2+}$  in solution in these soils.

The results also showed that although Ca and Mg uptake by rice is highly correlated with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  activity, a more pronounced relationship exists between uptake and the divalent activity ratios for these cations. This was believed to be due to competitive inhibition for uptake sites. This study also showed that Ca and Mg deficiencies in rice may be occurring on these soils.

Key words -  $\text{Ca}^{2+}$  activity, cation exchange, flooded soils, GEOCHEM,  $\text{Mg}^{2+}$  activity, mineral equilibria.

Although Ca and Mg are not directly involved in redox reactions in soils, their concentrations in the water soluble fraction have been shown to increase following flooding (Ponnamperuma, 1972; Van Breemen, 1975; Van Breemen, 1976). These increases have usually been attributed to exchange processes in which  $\text{Fe}^{2+}$  brought into solution by reduction reactions displaces  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  on the CEC. On the other hand, Van Breemen (1973) observed decreases in exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  following artificial oxidation of pyritic sediments. He attributed these decreases to increases in exchangeable  $\text{Al}^{3+}$  which resulted from the intense acidification brought on by aeration.

Lindsay (1979) suggested that  $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$  (lawsonite),  $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 7\text{H}_2\text{O}$  (leonhardite),  $\text{CaCO}_3$  (calcite), and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum) may be important in determining  $\text{Ca}^{2+}$  solubility in soils. He also indicated that exchange reactions were very important in maintaining  $\text{Ca}^{2+}$  in solution under acid and near neutral conditions. Van Breemen (1973) showed that most acid sulfate soils from Thailand were undersaturated with respect to gypsum and calcite. The soils that were found to be saturated with respect to these minerals were from the western part of the Bangkok Plain where river waters contain high concentrations of dissolved  $\text{Ca}^{2+}$ . Lindsay (1979) stated that most Mg minerals are too soluble to persist in soils with a pH below 7.5 and indicated that exchange reactions maintain the levels of  $\text{Mg}^{2+}$  in soil solution at low pH.

Much of the research on Ca and Mg uptake by rice has been of an indirect nature. Westfall et al. (1973) showed that rice plants grown with insufficient N supplies had lower Ca and Mg contents than their counterparts grown with adequate N. Otto et al. (1983), Benckiser et

al. (1984) and Howeler (1973) claimed that Ca and Mg play an important role in Fe toxicity in rice. They claimed that multiple nutritional stress was the main cause of Fe toxicity in rice. Benckiser et al. (1984) suggested that fertilization with N, P, K, Ca and Mg improved the Fe excluding mechanism of the plant, since root tissues had lower Fe and higher K, Ca and Mg than unfertilized plants. Howeler (1973) reported that the symptoms of Fe toxicity were inversely related to leaf content of P, K, Ca and Mg. Otto et al. (1983) ascribed Fe toxicity to insufficient supplies of K, P, Ca and Mg, rather than to high levels of active iron.

Rorison (1973) suggested that deficiencies of Ca and Mg were probably important factors associated with poor plant growth in acid sulfate soils. This was supported by Attanandana et al. (1982) who showed that Ca and Mg contents in plants grown on acid sulfate soils were highly correlated to dry matter production.

The objectives of this study were; (1) to measure the availability of Ca and Mg in flooded acid sulfate soils cropped to rice, (2) to try to determine what governs the solubility of these metals in these soils, and (3) to determine the relationships between Ca and Mg availability and uptake by rice.

#### MATERIALS AND METHODS

The results presented in this paper were obtained from a field study conducted on 134 flooded acid sulfate soils in the Central Plains region of Thailand and from a growth chamber study on 50 of the same soils. A complete description of the methods and materials used in these experiments is given in chapter two.

## RESULTS AND DISCUSSION

The negative log of  $\text{Ca}^{2+}$  activity ( $\text{pCa}^{2+}$ ) is plotted as a function of exchangeable Ca in Fig. 1. These data show that  $\text{Ca}^{2+}$  activities were significantly correlated with exchangeable Ca, indicating that exchange reactions may play an important role in governing  $\text{Ca}^{2+}$  solubility.

Lindsay (1979) stated that exchange reactions were very important in buffering solution  $\text{Ca}^{2+}$  in acid and near neutral soils. In a laboratory study in which acid sulfate soils that contained pyrite were artificially oxidized, Van Breemen (1973) found that decreases in exchangeable Ca brought on by acidification (Al exchange) were matched by increases in the water soluble fraction. Likewise, Ponnampetuma (1972), Van Breemen (1975 and 1976) indicated that increases in water soluble Ca were matched by decreases in the exchangeable fraction following flooding. They suggested that this was due to the production of  $\text{Fe}^{2+}$  under reduced conditions, followed by cation exchange.

The negative log of  $\text{Mg}^{2+}$  activity ( $\text{pMg}^{2+}$ ) is plotted as a function of exchangeable  $\text{Mg}^{2+}$  in Fig. 2. The highly significant correlation found between these variables indicates that exchange reactions may also play an important role in governing  $\text{Mg}^{2+}$  solubility in these soils. Exchange reactions have also been implicated as the mechanism for control of  $\text{Mg}^{2+}$  solubility in acid soils (Lindsay, 1979).

In order to determine if gypsum were controlling  $\text{Ca}^{2+}$  activities in these soils, the negative log of the ion activity product (pIAP) of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  was plotted as a function of the negative log of ionic strength as shown in Fig. 3. The linear trend shown by these data is indicative of the role  $\text{SO}_4^{2-}$  plays in determining ionic strength in acid sulfate soils. The solid line in this figure at  $\text{pIAP} = -4.64$

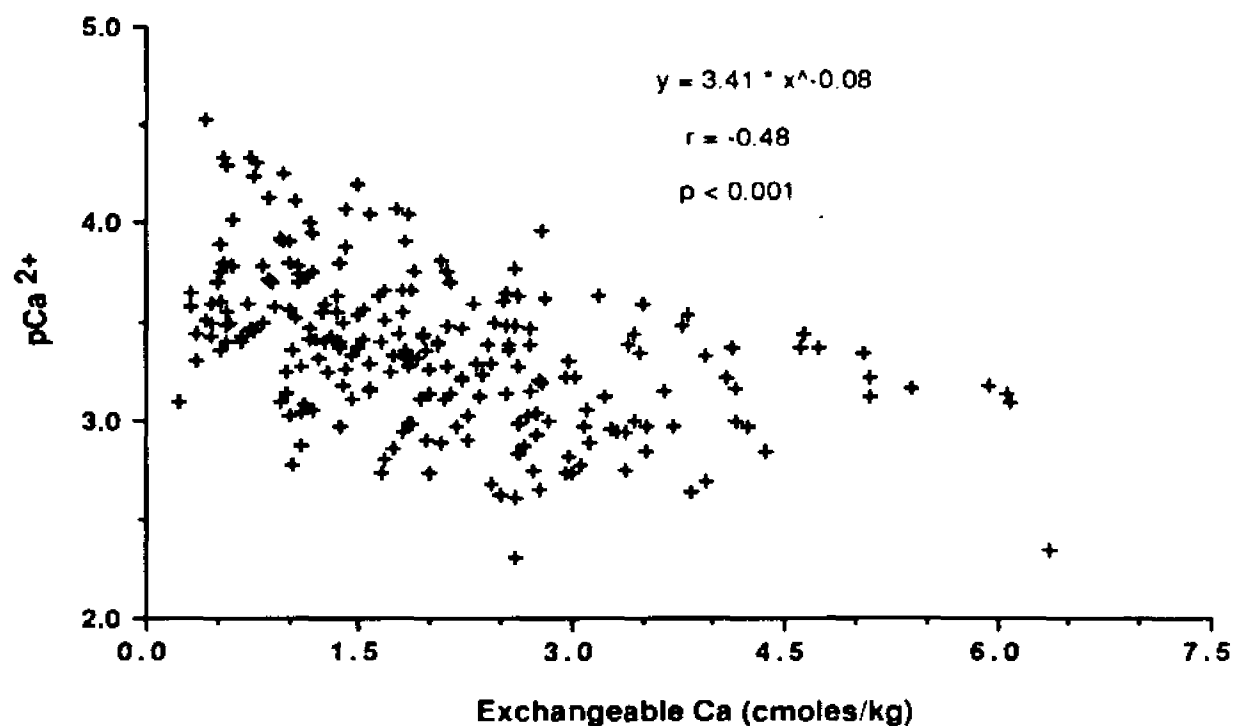


Fig. 1. The relationship between  $\text{Ca}^{2+}$  activity and exchangeable Ca in the growth chamber and field studies ( $n = 232$ ).

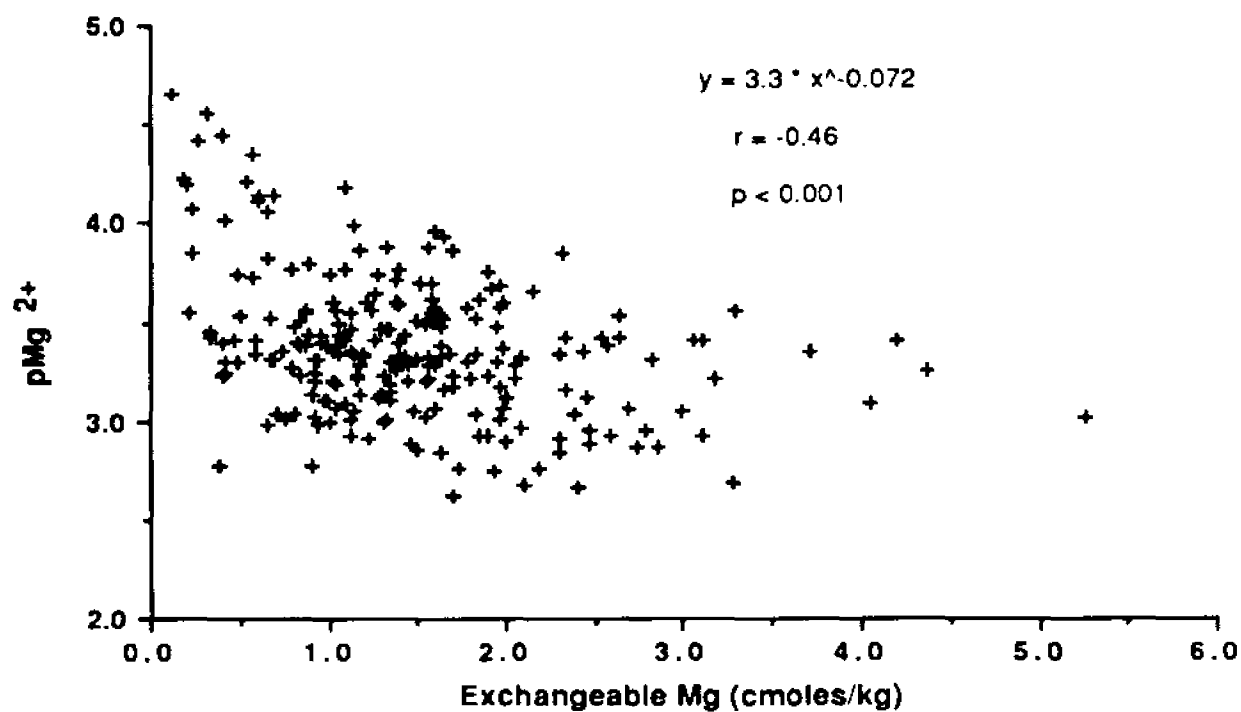


Fig. 2. The relationship between  $\text{Mg}^{2+}$  activity and exchangeable Mg in the growth chamber and field studies ( $n = 233$ ).



Table 1 - Ion activity products and equilibrium constants of selected Ca and Mg minerals.

Reaction	pIAP <sub>max</sub> *	pK <sup>†</sup>
$\beta\text{-CaSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Ca}^{2+} + \text{H}_4\text{SiO}_4^0$	-9.10	-13.3
$\text{CaMg}(\text{SiO}_3)_2 + 4\text{H}^+ + 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{Mg}^{2+} + 8\text{H}_4\text{SiO}_4^0$	-20.0	-21.2
$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	7.80	8.41
$\text{MgCO}_3 = \text{Mg}^{2+} + \text{CO}_3^{2-}$	7.90	7.46
$\text{MgSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} = \text{Mg}^{2+} + \text{H}_4\text{SiO}_4^0$	-9.00	-11.4
$\text{Mg}_2\text{SiO}_4 + 4\text{H}^+ = 2\text{Mg}^{2+} + \text{H}_4\text{SiO}_4^0$	-20.7	-28.9
$\text{Mg}_{1.6}\text{Fe(II)}_{0.4}\text{SiO}_4 + 4\text{H}^+ = 1.6\text{Mg}^{2+} + 0.4\text{Fe}^{2+} + \text{H}_4\text{SiO}_4^0$	-20.1	-26.2
$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 3\text{Mg}^{2+} + 3\text{H}_4\text{SiO}_4^0$	-27.0	-32.9
$\text{Mg}_2\text{SiO}_6(\text{OH})_4 + 2\text{H}_2\text{O} + 4\text{H}^+ = 2\text{Mg}^{2+} + 3\text{H}_4\text{SiO}_4^0$	-15.3	-15.9
$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 2\text{H}_2\text{O} + 2\text{H}_2\text{O} + 6\text{H}^+ = 3\text{Mg}^{2+} + 4\text{H}_4\text{SiO}_4^0$	-24.3	-30.4
$\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8 + 12\text{H}^+ = 6\text{Mg}^{2+} + 4\text{H}_4\text{SiO}_4^0 + 2\text{H}_2\text{O}$	-59.5	-61.8

\* - negative log of ion activity product (maximum observed)

† - taken from Lindsay (1979)

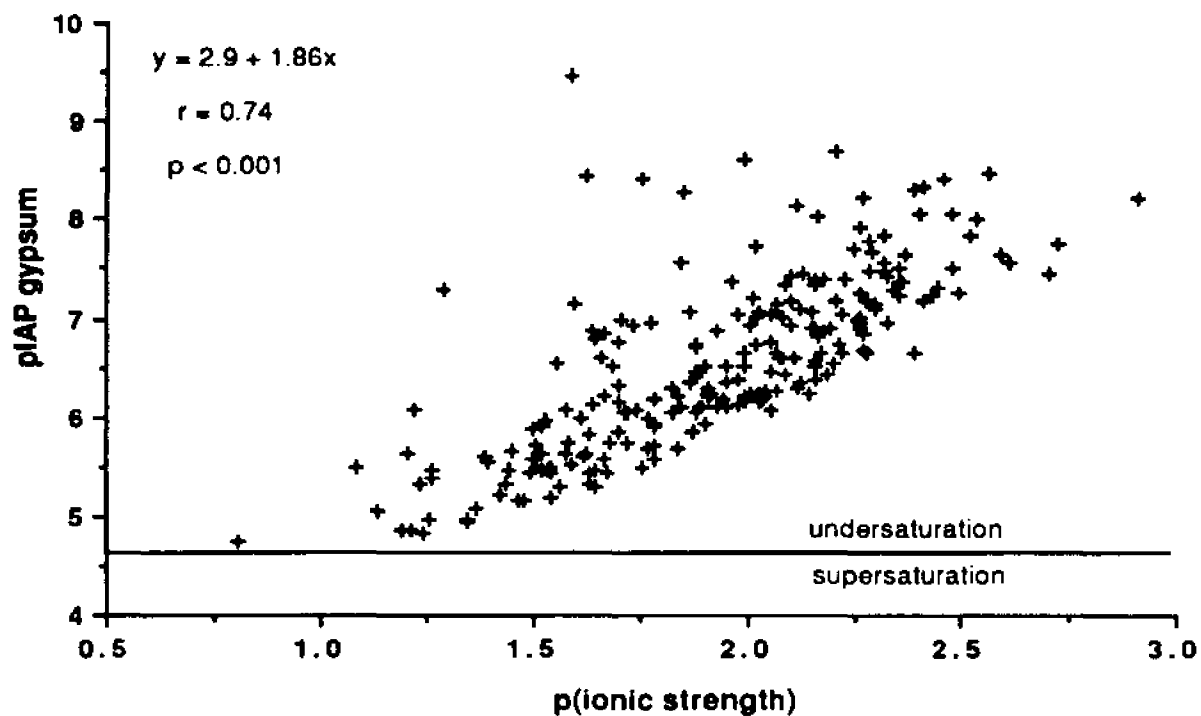


Fig. 3. The relationship between pIAP of gypsum and ionic strength in the growth chamber and field studies ( $n = 234$ ).

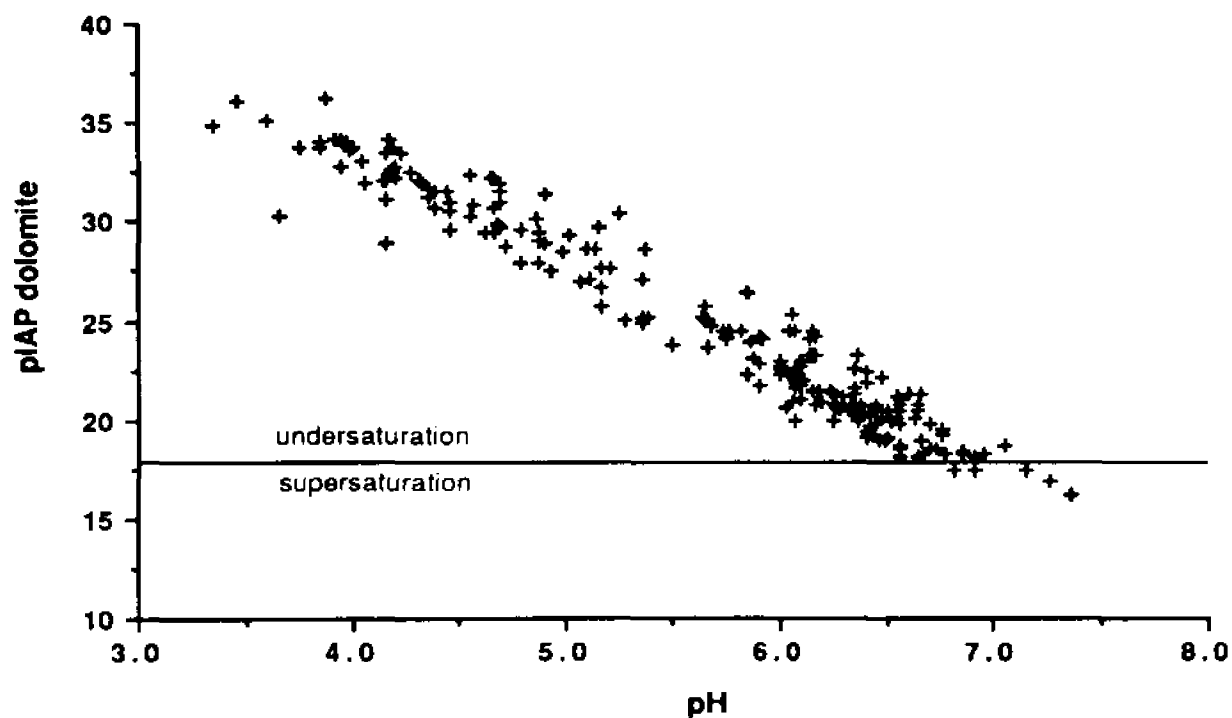


Fig. 4. The relationship between pIAP of dolomite and pH in the growth chamber and field studies ( $n = 234$ ).

corresponds to the solubility of gypsum (Lindsay, 1979). Since these data indicate undersaturation with respect to gypsum, it is an unlikely candidate for controlling solution  $\text{Ca}^{2+}$  in the soils studied. However, under very dessicating conditions, such as that found in the Central Plains region of Thailand during the dry season, gypsum precipitation may occur. Van Breemen (1973) stated that the persistence of gypsum in soils under humid conditions was often seasonal; being dependent upon relatively dry conditions.

The IAP of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) is plotted as a function of pH in Fig. 4. These data indicate that dolomite was probably not responsible for the measured solubilities of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  under acidic conditions, however above pH 6.5 this phase may have governed the solubilities of these ions.

Solubility calculations for some other Ca and Mg minerals are shown in Table 1. These data indicate undersaturation was found with respect to most Ca and Mg carbonates and silicates in the growth chamber and field studies. It was not possible to determine if these soils were in equilibrium with leonhardite and lawsonite since the only thermodynamic data available for these mineral phases is highly questionable (Lindsay, 1979). These data support the predictions made by Lindsay (1979), who indicated that most Ca and Mg minerals were too soluble to persist in acid soils.

In light of the data shown in Table 1, and the highly significant relationships found between  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  activities and exchangeable  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , exchange reactions were suspected as the mechanism governing the solubility of these ions. Therefore,  $\text{E}'\text{-Ca}$  (the divalent

cationic charge fraction in the soil solution accounted for by  $\text{Ca}^{2+}$ ) was plotted as a function of E-Ca (the divalent cationic charge fraction on the CEC accounted for by  $\text{Ca}^{2+}$ ) as shown in Fig. 5. This figure represents an exchange isotherm in which  $\text{Ca}^{2+}$  is being exchanged for other divalent metals (in this case, the metals are  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$ ). The thermodynamic non-preference isotherm is represented by the solid line that makes a 45 degree angle with both coordinate axis (Sposito, 1981). These data provide strong evidence that  $\text{Ca}^{2+}$  activities in flooded acid sulfate soils are regulated by cation exchange reactions.

The divalent charge fraction in the soil solution attributable to  $\text{Mg}^{2+}$  (E'-Mg) is plotted as a function of that on the CEC due to Mg (E-Mg) in Fig. 6. These data indicate that  $\text{Mg}^{2+}$  activities were higher than would be predicted on the basis of non-preferential cation exchange. However, the linear trend shown in this figure indicates that exchange reactions are probably important in governing  $\text{Mg}^{2+}$  activities. In a laboratory study, Van Breemen (1973) showed that after artificial oxidation of acid sulfate soils, the concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  increased in the water soluble fraction. He indicated that this increase was due to exchange reactions with  $\text{Al}^{3+}$  produced under the highly acidic conditions. The increases in the water soluble fractions of these metals were accompanied by decreases in the exchangeable fraction. He calculated that while the total increase in dissolved  $\text{Ca}^{2+}$  and  $\text{Na}^+$  came from exchange reactions, only 65% of the  $\text{Mg}^{2+}$  could be accounted for by this process and the remaining 35% must have originated from Mg-bearing minerals. He concluded that kaolinite formation at the expense of Mg-montmorillonite was the source of the extra  $\text{Mg}^{2+}$ .

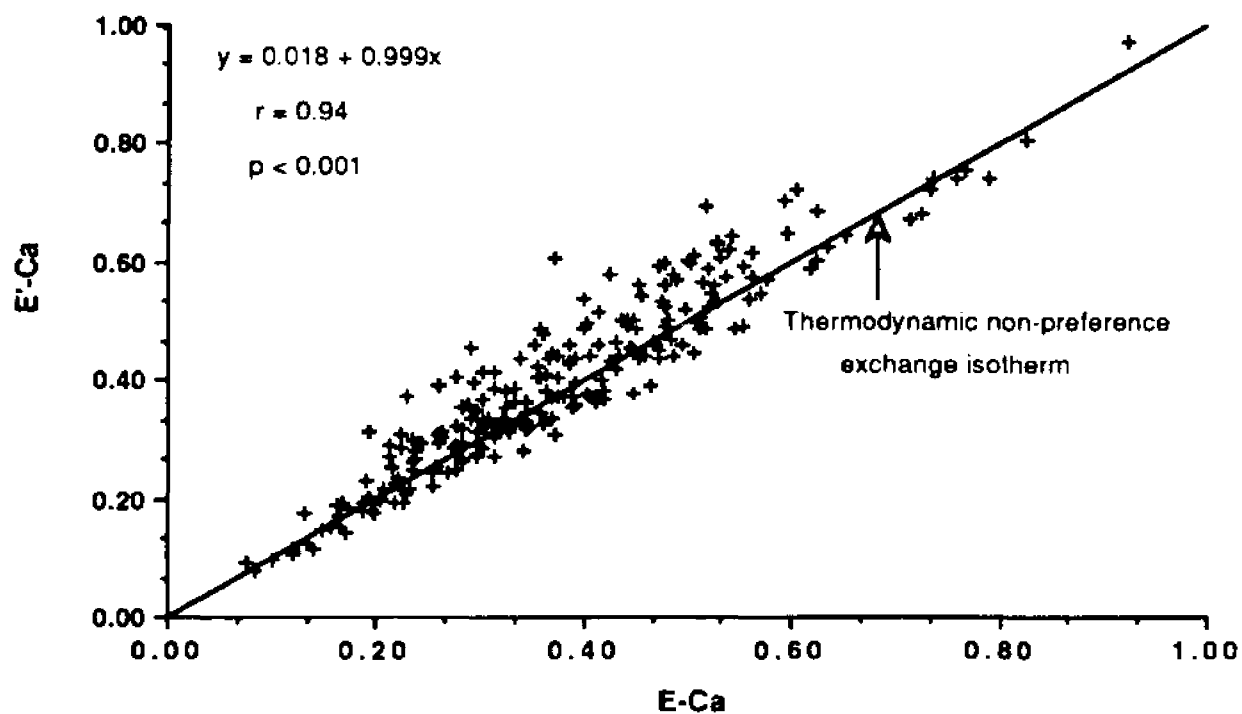


Fig. 5. The relationship between  $E'-Ca$  and  $E-Ca$  in the growth chamber and field studies ( $n = 233$ ).

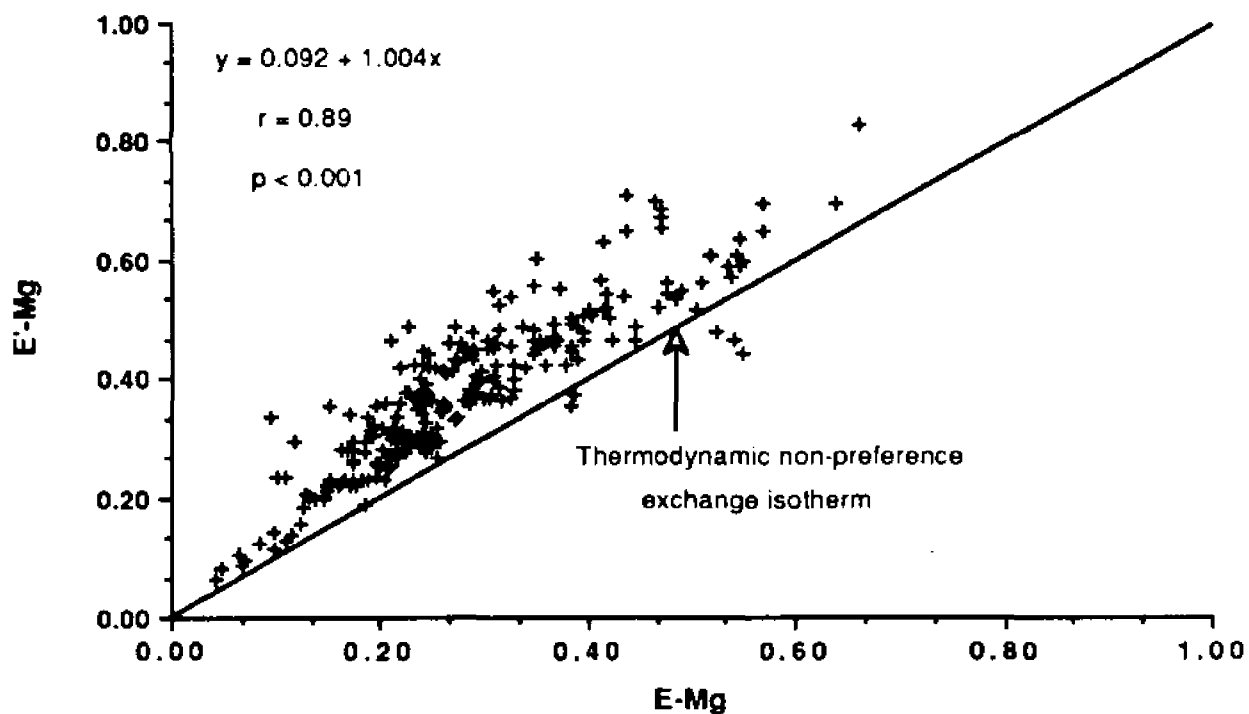


Fig. 6. The relationship between  $E'-Mg$  and  $E-Mg$  in the growth chamber and field studies ( $n = 233$ ).

However, this claim could not be substantiated in later studies (Van Breemen, 1976). Later, Van Breemen (1980) suggested that  $Mg^{2+}$  replacement by  $Fe^{3+}$  in smectite minerals (conversion of nontronite to saponite) may have been the source of the extra  $Mg^{2+}$ .

This hypothesis could not be tested in this study due to a lack of thermodynamic data for nontronite and saponite.

In conclusion, it appears that exchange reactions are responsible for observed  $Ca^{2+}$  activities and partly responsible for  $Mg^{2+}$  activities in acid sulfate soils. Other sources of Mg (possibly clay minerals) probably contribute to the  $Mg^{2+}$  in solution.

#### CALCIUM AND MAGNESIUM UPTAKE - GROWTH CHAMBER EXPERIMENT

Calcium uptake is plotted as a function of  $pCa^{2+}$  in Fig. 7. The highly significant correlation shown by these data indicates that Ca uptake increased with increases in  $Ca^{2+}$  activity, as would be expected.

Calcium uptake is plotted as a function of  $E'-Ca$  in Fig. 8. The higher correlation coefficient indicates that  $E'-Ca$  was more closely related to Ca uptake than  $Ca^{2+}$  activity. This was also shown to be the case for Fe uptake (chapter two) and Mn uptake (chapter three). This was believed to be due to competitive inhibition for uptake sites by ions of similar charge. Adams (1966) and Bennett and Adams (1970) found that Ca/total-cation molar activity ratios were better indicators of Ca deficiency than  $Ca^{2+}$  activities alone. Although they did not measure Ca uptake, they found that activity ratios of less than 0.15 resulted in decreased growth of shoots and roots. Based on their results and the results found in this study, it appears that activity ratios are better

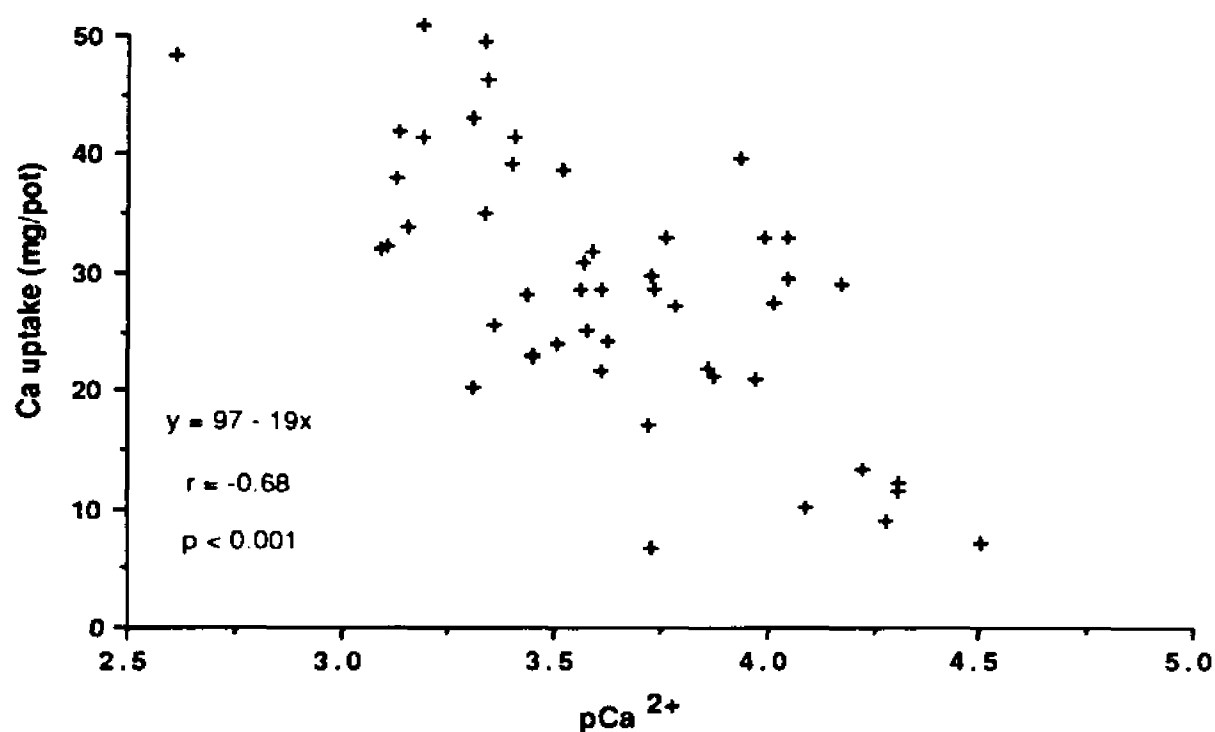


Fig. 7. The relationship between Ca uptake and Ca<sup>2+</sup> activity in the growth chamber study (n = 49).

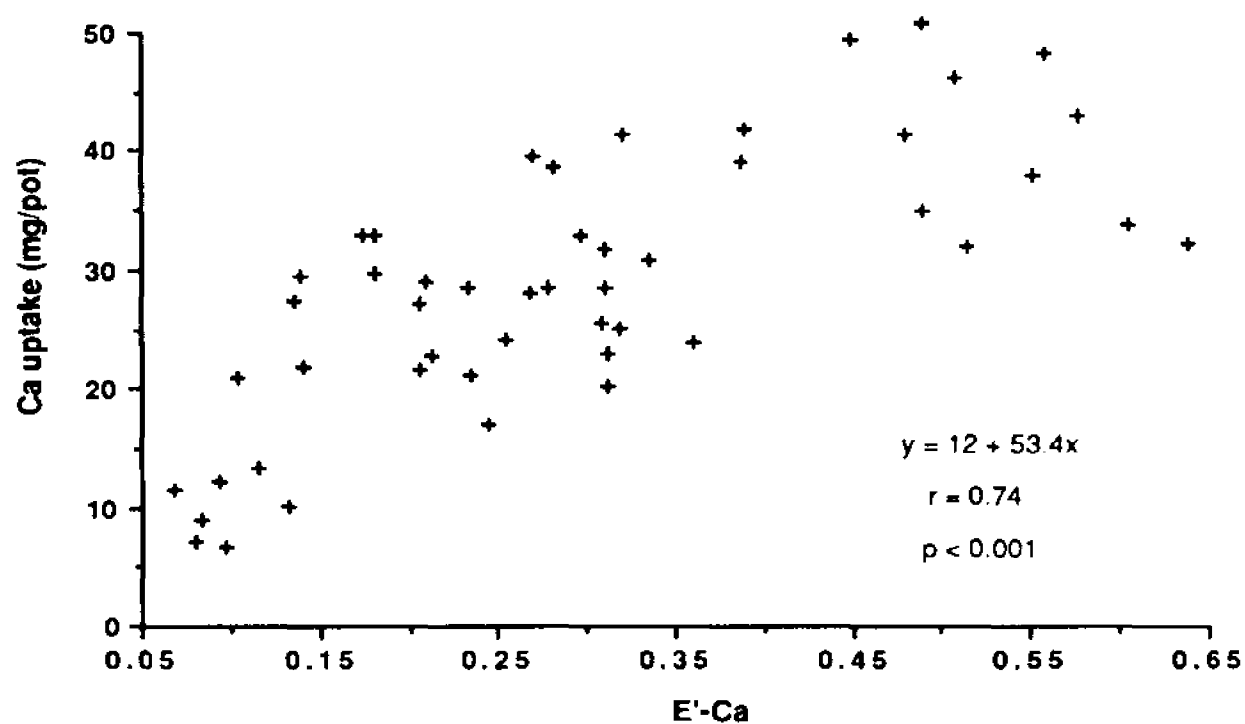


Fig. 8. The relationship between Ca uptake and E'-Ca in the growth chamber study (n = 49).

availability indices for metals than single ion activities since they reflect ion competition.

Calcium and Mg uptake is plotted as a function of leaf Ca and Mg contents in Figs. 9 and 10, respectively. These figures were included in order to show that leaf concentrations were related to uptake, since dry matter production was not determined under field conditions.

Magnesium uptake is plotted as a function of  $pMg^{2+}$  in Fig. 11. These data indicate that Mg uptake was significantly correlated with  $Mg^{2+}$  activity, as would be expected. Magnesium uptake is plotted as a function of  $E'-Mg$  in Fig. 12. These data indicate that Mg uptake was more closely related to  $E'-Mg$  than  $Mg^{2+}$  activity. This was also shown to be the case for Ca, Fe, and Mn. The reasons for this are discussed above.

#### FIELD STUDY

Leaf Ca contents observed in the field study are plotted as a function of  $E'-Ca$  in Fig. 13. These data indicate that Ca uptake in the field followed the same trends as that found in the growth chamber study. The correlation between leaf Ca and  $E'-Ca$  ( $r=.60$ ) was also much better than that between leaf Ca and  $Ca^{2+}$  activity ( $r=.44$ ), providing further evidence that activity ratios are better availability indices for metal uptake by rice than activity alone. Leaf Ca contents observed in the field study varied from 0.087 to 0.79%, with an average of 0.26%. Calcium deficiencies may have occurred since the reported critical Ca level in rice is 0.15% (Tanaka and Yoshida, 1970). The mean leaf Ca value was comparable to that found by Westfall et al. (1973) in the Y-leaves of healthy rice (0.24%).



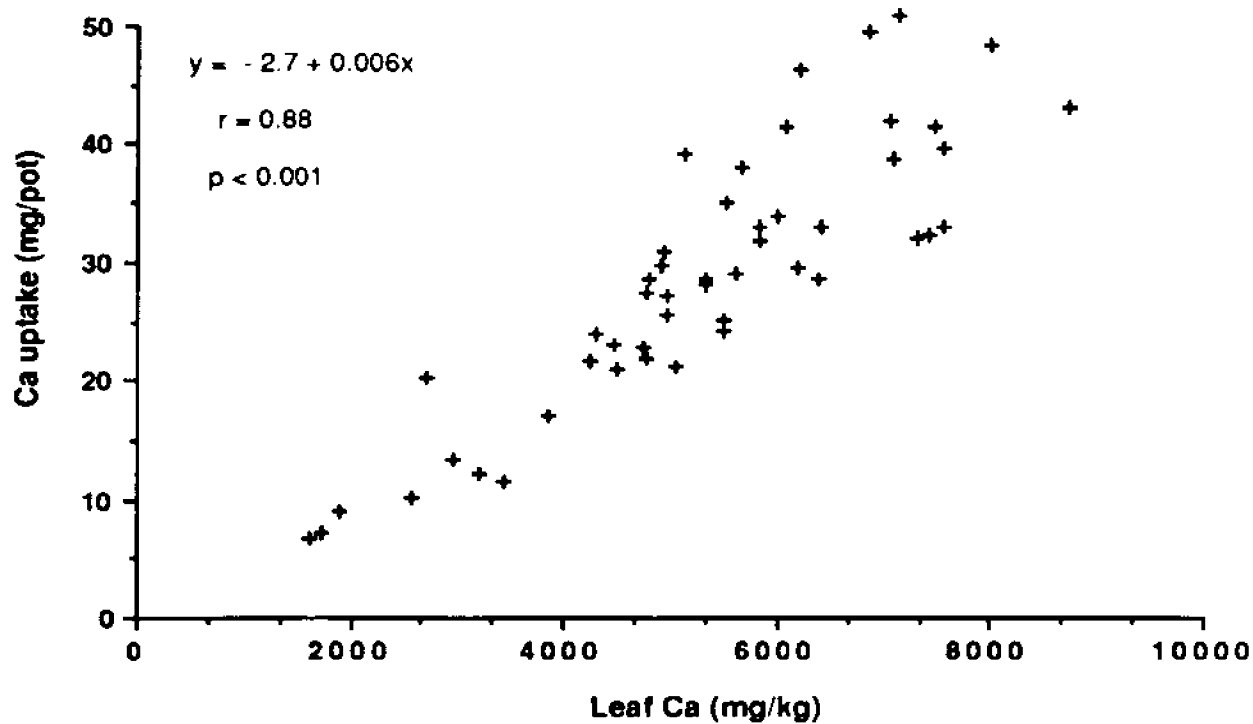


Fig. 9. The relationship between Ca uptake and leaf Ca in the growth chamber study ( $n = 49$ ).

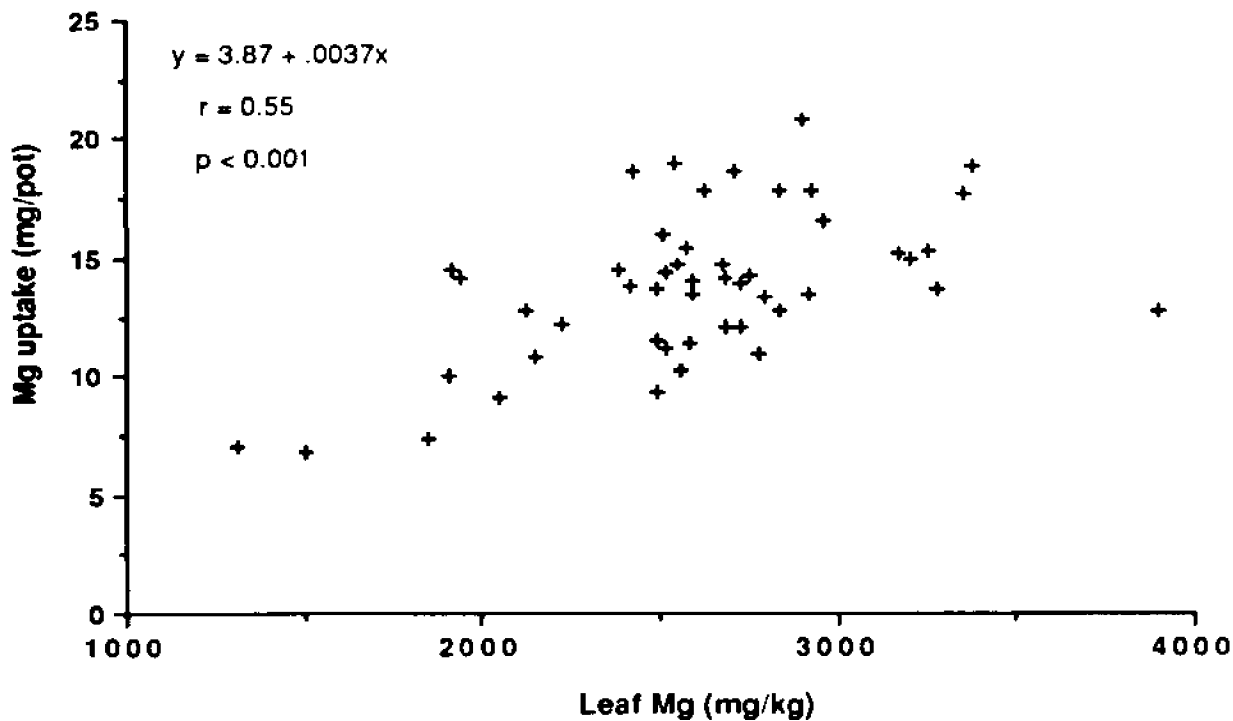


Fig. 10. The relationship between Mg uptake and leaf Mg in the growth chamber study ( $n = 49$ ).

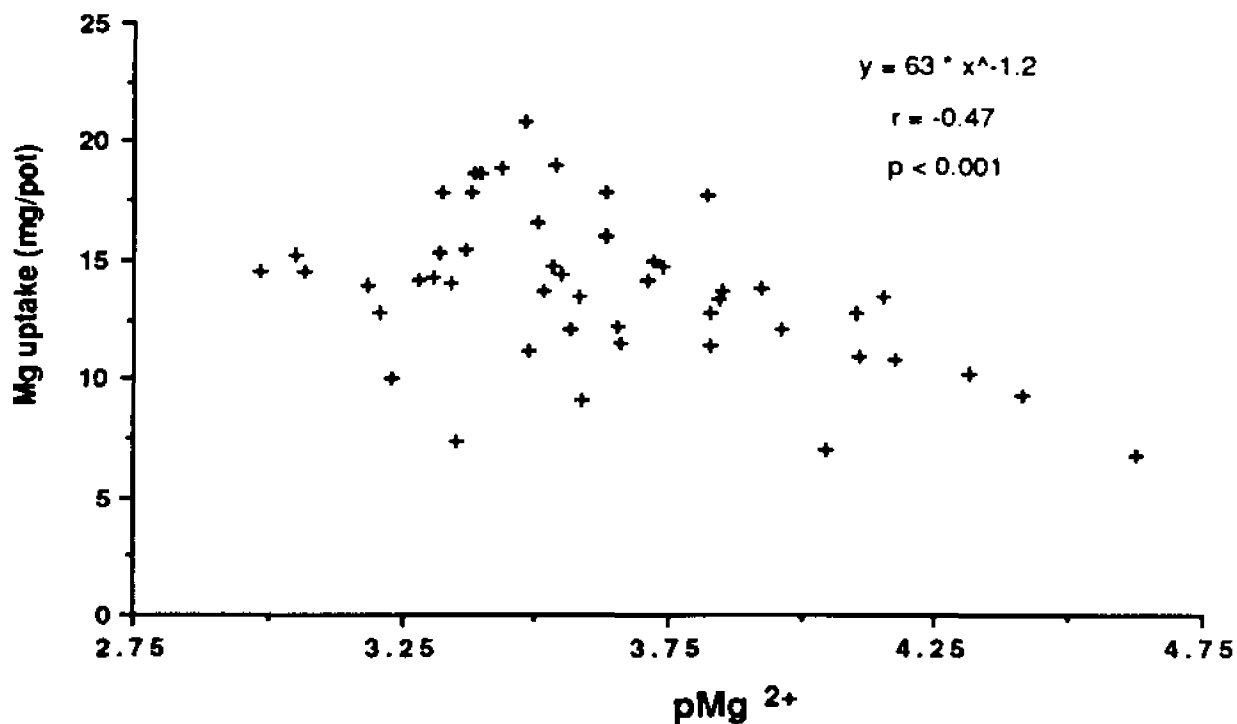


Fig. 11. The relationship between Mg uptake and  $\text{Mg}^{2+}$  activity in the growth chamber study ( $n = 49$ ).

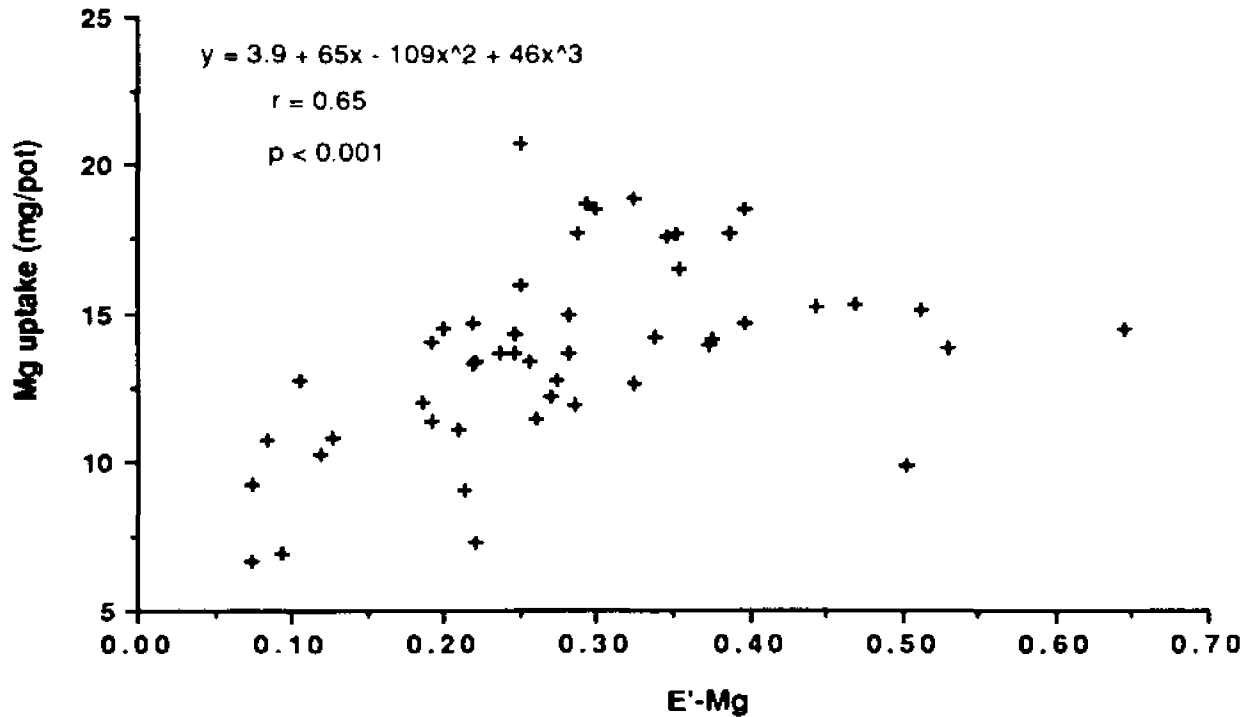


Fig. 12. The relationship between Mg uptake and  $E'-\text{Mg}$  in the growth chamber study ( $n = 49$ ).

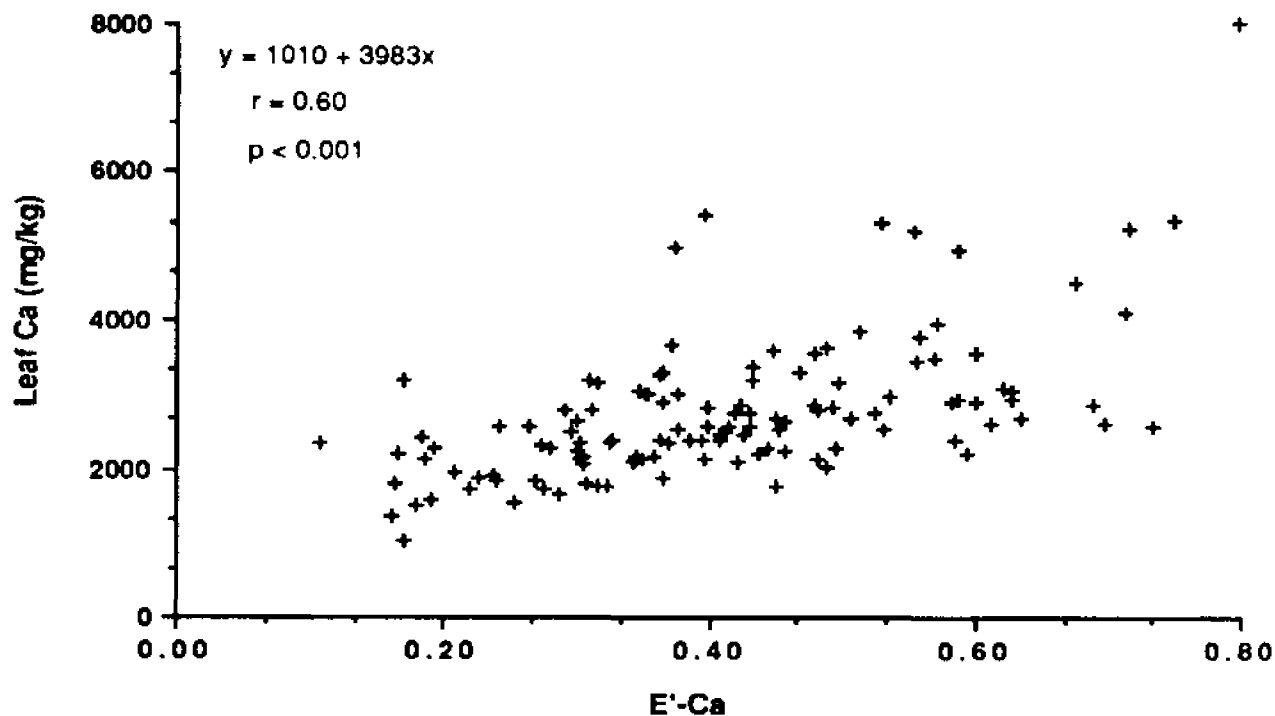


Fig. 13. The relationship between leaf Ca and  $E'-Ca$  in the field study ( $n = 126$ ).

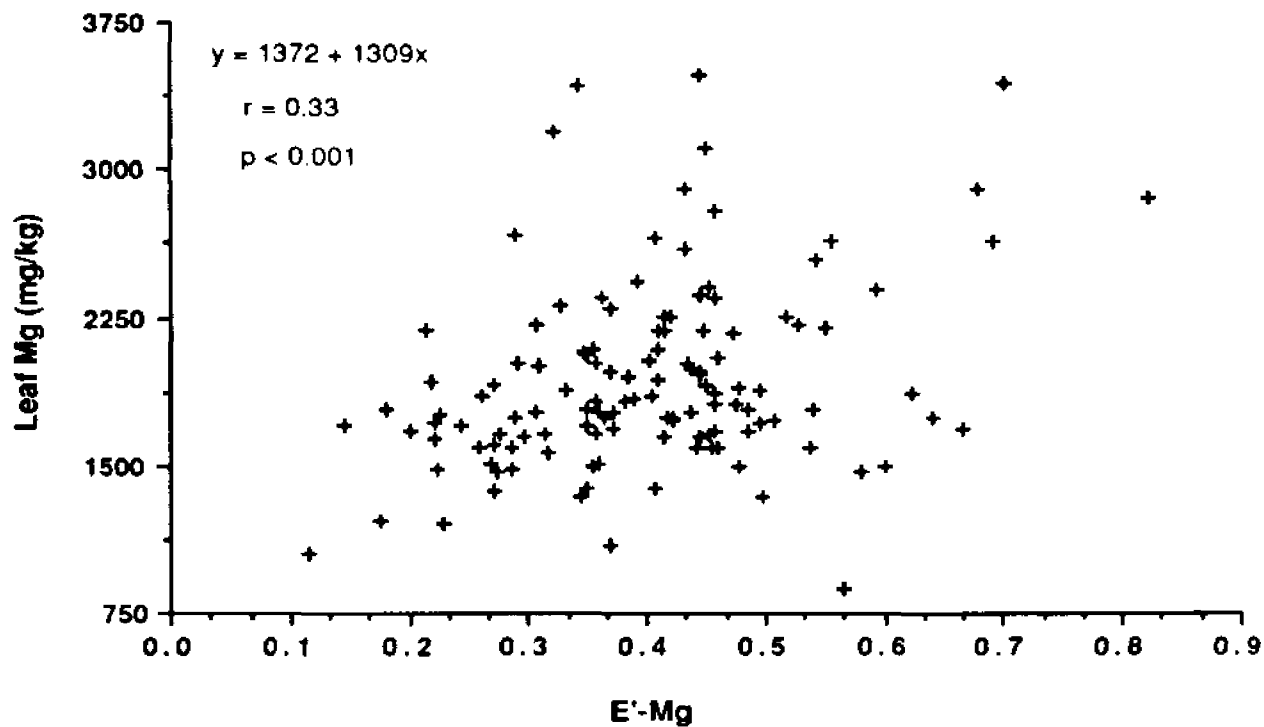


Fig. 14. The relationship between leaf Mg and  $E'-Mg$  in the field study ( $n = 126$ ).

Leaf Mg is plotted as a function of  $E'-Mg$  in Fig. 14. These data indicate that leaf Mg was significantly correlated with  $E'-Mg$ , indicating Mg uptake trends under field conditions were similar to that observed in the growth chamber experiment. Leaf Mg varied from 0.080 to 0.34%, with a mean of 0.19%. Magnesium deficiencies may have occurred since the critical Mg level in rice reported by Tanaka and Yoshida (1970) was 0.10%. The mean leaf Mg observed in the field was comparable to that found by Westfall et al. (1973) in healthy rice V-leaves (0.18%).

#### CONCLUSIONS

The results of this study support the hypothesis that exchange reactions govern the solubility of  $Ca^{2+}$  and to a large degree  $Mg^{2+}$  in acid soils. However, Mg-bearing minerals may also contribute to  $Mg^{2+}$  in solution in acid sulfate soils.

The results also showed that although Ca and Mg uptake by rice was significantly correlated with  $Ca^{2+}$  and  $Mg^{2+}$  activity, a more pronounced relationship existed between uptake and the divalent activity ratios for these cations. This was believed to be due to competitive inhibition for uptake sites. Leaf metal analyses indicated that Ca and Mg deficiencies in rice may be occurring on these soils.

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## Chapter Five

### Aluminum Availability and Uptake by Rice in Acid Sulfate Soils

## ABSTRACT

Aluminum availability and uptake by rice were evaluated in 134 flooded acid sulfate soils in the Central Plains region of Thailand and in a growth chamber study using 50 of the same soils. Soil and plant metal analyses were conducted at the panicle differentiation stage of growth in both studies and in the soil prior to transplanting in the growth chamber study. Metal activities were determined from free metal concentrations using GEOCHEM and activity coefficients using the Davies equation. Exchangeable metals were determined from sodium acetate extracts buffered to the soil pH.

Activities of  $\text{Al}^{3+}$  in flooded acid sulfate soils were found to be negatively correlated with pH. The mineral phases believed to be governing  $\text{Al}^{3+}$  activities were jarvanite under low pH conditions and amorphous  $\text{Al}(\text{OH})_3$  at high pH. Large quantities of exchangeable Al were observed and appeared to be in equilibrium with Al in solution. It was hypothesized that solution  $\text{Al}^{3+}$  in these soils is not only controlled by precipitation/dissolution reactions, but adsorption/desorption as well.

Mortality of rice associated with Al toxicity was observed under field and growth chamber conditions. Although  $\text{Al}^{3+}$  activities were not correlated with leaf Al contents, they were found to be negatively correlated to leaf P contents. This phenomenon was believed to be due to P precipitation by Al, as most of the soils studied were strongly supersaturated with respect to variscite.

Key words -  $\text{Al}^{3+}$  activity, amorphous  $\text{Al}(\text{OH})_3$ , cation exchange, flooded soils, GEOCHEM, jarvanite, mineral equilibria, variscite.



Various solid phases have been implicated in the control of Al solubility in soils. Lindsay et al. (1959) and Richburg and Adams (1970) suggested that gibbsite or a gibbsite-like mineral controls Al solubility. Marion et al. (1974) concluded that gibbsite, halloysite, kaolinite or montmorillonite may govern Al solubility, depending on the soil. Van Breemen (1973) suggested that basic aluminum sulfates may control Al solubility in acid sulfate soils. This hypothesis was supported by Nordstrom (1982), who claimed that  $\text{KAl}_3(\text{SO}_4)_2(\text{OH}) \cdot 5\text{H}_2\text{O}$  (alunite),  $\text{Al}(\text{SO}_4)\text{OH} \cdot 5\text{H}_2\text{O}$  (turbanite) and  $\text{Al}_4(\text{SO}_4)_{10} \cdot 5\text{H}_2\text{O}$  (basaluminite) were likely to control Al solubility under acidic conditions if  $\text{SO}_4^{2-}$  activities were high enough.

Although there are many unanswered questions concerning which mineral phase is controlling Al solubility in soils, there is no doubt that Al toxicity is a major problem in acid soils. Aluminum toxicity in rice has been reported by several workers (Cate and Sukhai, 1964; Nhung and Ponnampuruma, 1966; Tanaka and Naversero, 1966; Thawornwong and Van Diest, 1974; Tomlinson, 1957). However, values reported for the amount of Al in solution required to induce injury and/or mortality in rice are quite variable (Cate and Sukhai, 1964). Workers studying Al toxicity have often demonstrated that plant injury is more dependant on the activities of certain Al species than the total amount present (Alva et al., 1986; Adams and Lund, 1966; Paven et al., 1982). Paven et al. (1982) showed decreases in the relative root growth of coffee grown in acid soils were more closely related to  $\text{Al}^{3+}$  activity than total water soluble Al or percent Al saturation of the CEC.

Alva et al. (1986) found that root elongation in four plant species subjected to injurious levels of Al in solution was increased by

increasing P/Al molar ratios. However, they attributed the beneficial effect of P to decreases in monomeric Al in solution. On the other hand, interference in P uptake and/or assimilation has been suggested as the mechanism of Al toxicity in rice. Phosphorus precipitation in the media, on the roots, and/or in the roots as aluminum phosphate has been considered the process through which this mechanism operates (Tanaka and Navarero, 1966).

The objectives of this study were (1) to measure the solubility of Al under natural conditions in flooded acid sulfate soils with a wide range in acidity, (2) to try to determine what controls Al solubility in these soils, and (3) to determine the effects of Al on the nutrient status of rice.

#### METHODS AND MATERIALS

The results presented in this chapter were obtained from a field study conducted on 134 flooded acid sulfate soils in the Central Plains region of Thailand and from a growth chamber study on 50 of the same soils. A complete description of the methods and materials used in these studies is given in chapter two.

## RESULTS AND DISCUSSION

The negative log of  $\text{Al}^{3+}$  activity ( $\text{pAl}^{3+}$ ) is plotted as a function of pH in Fig. 1. As would be expected,  $\text{pAl}^{3+}$  was found to be positively correlated to pH. It should be mentioned that under acidic conditions (3.2 to 5.2), the predicted concentrations of aluminum sulfate complexes were generally higher than that for the free metal (data not shown).

In Fig. 2,  $\text{pAl}(\text{OH})_3$  is plotted as a function of  $2\text{pH} + \text{pSO}_4^{2-}$ . From this figure, it would appear that jurbanite or some type of basic aluminum sulfate is controlling Al solubility at low to medium pH values (3.5 to 6.0). At the higher pH range, and at lower sulfate activities, amorphous  $\text{Al}(\text{OH})_3$  seems to provide the limits of Al solubility in these soils.

Van Breemen (1973) provided evidence indicating that a basic aluminum sulfate ( $\text{pK} = 17.2$ ) determined the upper limit of dissolved Al in acid sulfate soils and acid mine spoils. Nordstrom (1982) supported these findings and proposed that the solid phase controlling Al solubility in natural waters was dependent on both pH and  $\text{SO}_4^{2-}$  activity. He indicated that jurbanite provided the upper limits for  $\text{Al}^{3+}$  solubility in acid soils, depending upon  $\text{SO}_4^{2-}$  activity. At higher pH's alunite or gibbsite would be the controlling phase outlined in his scheme. He also calculated that the solubility product of jurbanite ( $\text{pK} = 17.8$ ) was close to that of Van Breemen's basic aluminum sulfate and concluded that they were probably one and the same. The data shown in Fig. 2 appear to conform to the results found by Van Breemen (1973) and the paradigm set forth by Nordstrom (1982), with jurbanite and amorphous  $\text{Al}(\text{OH})_3$  being the dominant phases at the pH's and  $\text{SO}_4^{2-}$  activities observed in this study.

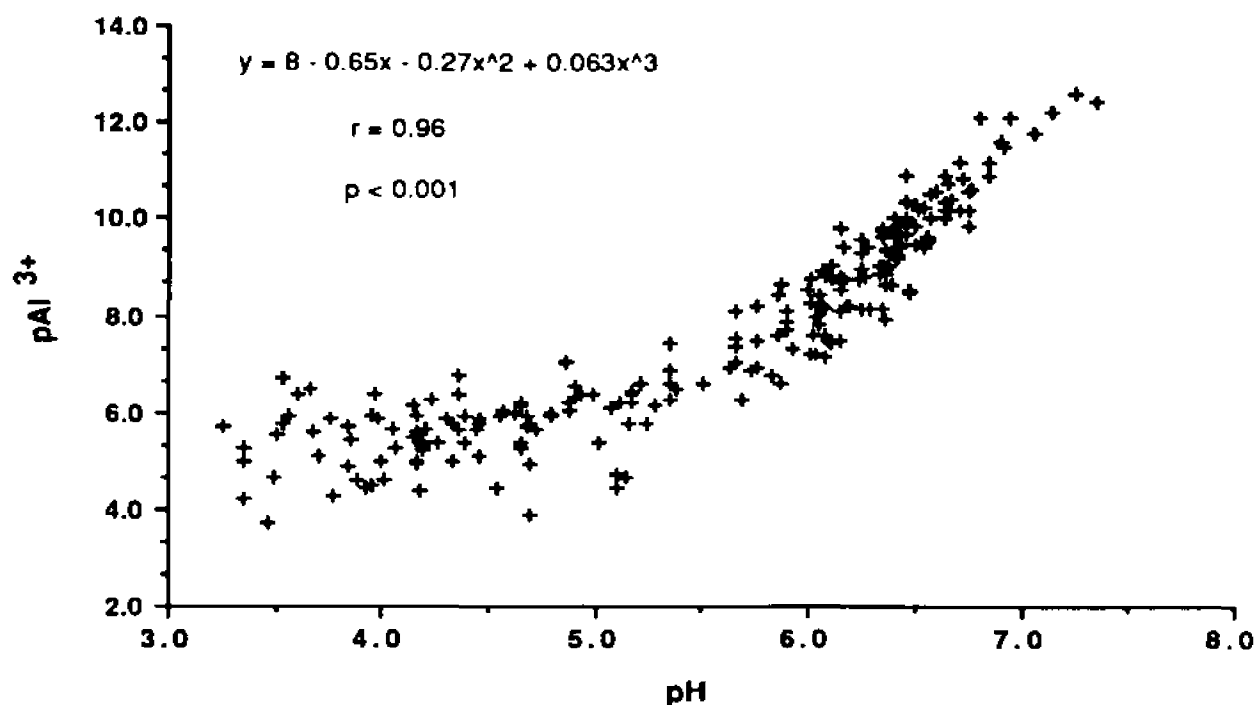


Fig. 1. The relationship between  $Al^{3+}$  activity and pH in the growth chamber and field studies ( $n = 234$ ).

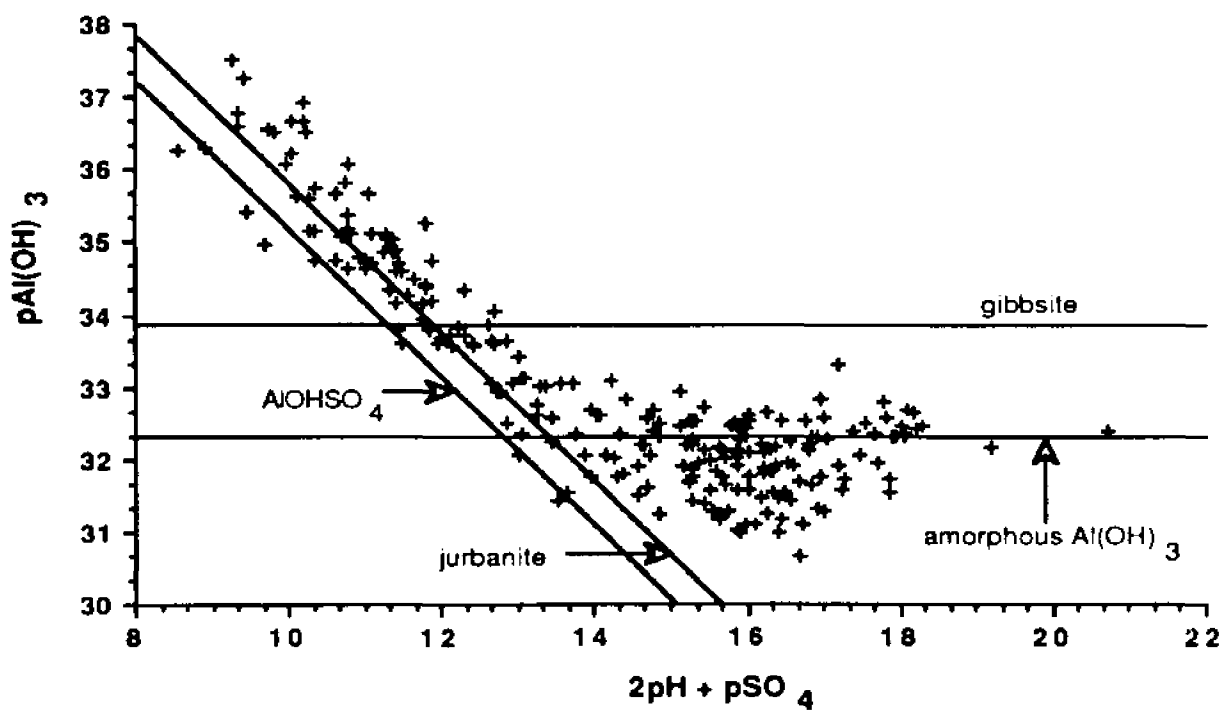


Fig. 2. The relationship between  $pAl(OH)_3$  and  $2pH + pSO_4^{2-}$  in the growth chamber and field studies ( $n = 234$ ), with theoretical solubility isotherms for some Al minerals.

Adsorption is probably another important control mechanism governing Al solubility. However, with our current knowledge and technology it is impossible to determine whether adsorption or precipitation phenomena are responsible for measured solubilities of a particular chemical moiety. In Fig. 3, exchangeable Al is plotted as a function of pH. As expected, exchangeable Al increased with decreases in soil pH. Homovalent exchange isotherms analagous to those made for Fe (chapter two), Mn (chapter three) Ca, and Mg, (chapter four) could not be made since there was not another trivalent cation in these soils at measureable concentrations. Since exchangeable H and Na were not determined, heterovalent exchange isotherms were also not possible.

One possible geochemical route for Al in acid sulfate soils which undergo alternate periods of wetting and drying would involve both adsorption/desorption and precipitation/dissolution reactions, which are linked to the pH-redox status of the soil. On this hypothetical highway, aluminum hydroxides such as gibbsite or amorphous  $\text{Al}(\text{OH})_3$  would began to dissolve as acid is produced following oxidation at the beginning of the dry season. As  $\text{Al}^{3+}$  activites increase,  $\text{Al}^{3+}$  would replace other cations such as Ca, Mg and Mn on the CEC as described by Van Breemen (1973). This process would continue until the activities of  $\text{Al}^{3+}$  and  $\text{SO}_4^{2-}$  reached the point of jarvanite saturation, at which time precipitation of this mineral phase would begin. However, before this process could be fully initiated, large quantities of Al in solution would be removed by exchange processes, buffering the amount in solution. The amount of Al held on the CEC would not only be dependent on the  $\text{Al}^{3+}$  activity, but on the magnitude and nature of the CEC.

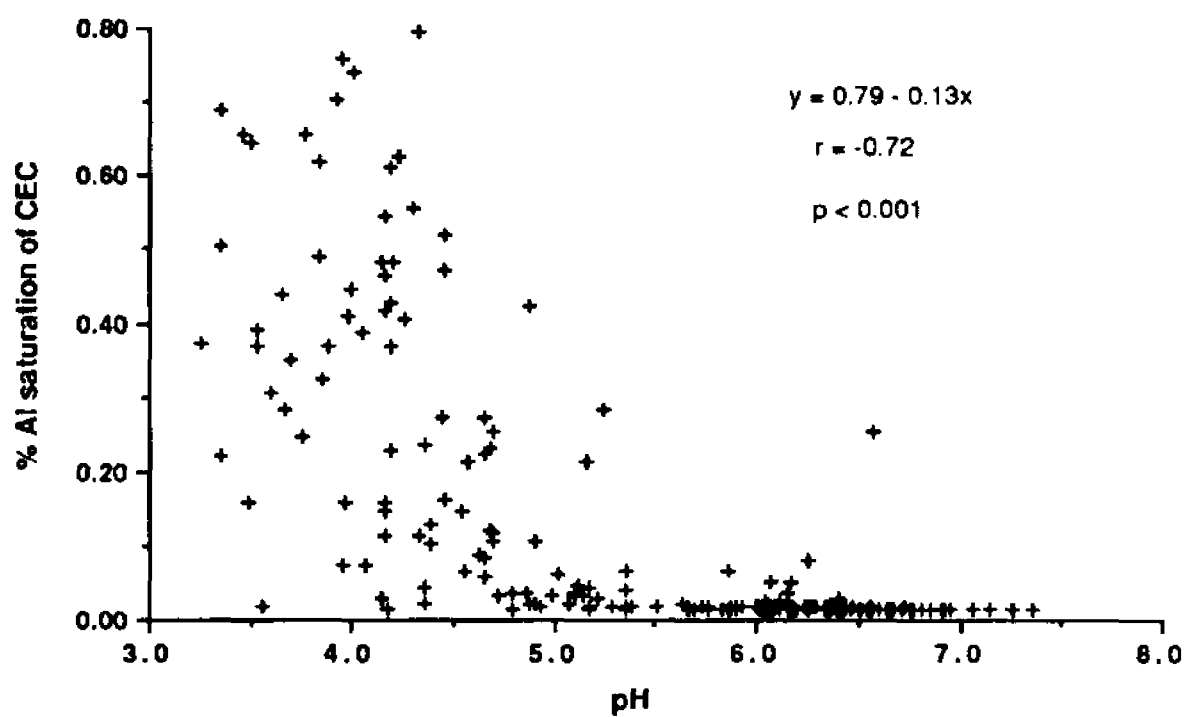


Fig. 3. The relationship between the % Al saturation of the CEC and pH in the growth chamber and field studies (n = 233).

When the rains return at the beginning of the monsoon season, the redox of the soil would decrease due to flooding. This would result in the reduction of Fe oxides and hydroxides which would, in turn, cause increases in pH. With increases in pH, jurbanite would become metastable with respect to Al hydroxides such as amorphous  $\text{Al}(\text{OH})_3$ , which would then begin to precipitate. However, as  $\text{Al}^{3+}$  disappeared from solution it would be replaced by Al on the CEC until a new equilibrium was reached. This release of  $\text{Al}^{3+}$  from the CEC would consume hydroxide and buffer the pH and thus the  $\text{Al}^{3+}$  activity until most of the Al on the CEC had been inactivated. Al hydroxide precipitation would probably occur until the end of the monsoon season, at which time the cycle would be repeated.

The hypothetical pathway described above would only be operable if exchange reactions were occurring faster than precipitation reactions. Another prerequisite for this pathway would be near equilibrium conditions between  $\text{Al}^{3+}$  in solution and that on the CEC. Evidence indicating that  $\text{Al}^{3+}$  activities are in at least a pseudo-equilibrium with exchangeable Al is presented in Fig. 4. In this figure, Al saturation of the CEC is plotted as a function of  $\text{pAl}^{3+}$ . These data indicate that Al saturation was directly related to  $\text{Al}^{3+}$ , providing evidence that they are in equilibrium.

#### PLANT UPTAKE

Aluminum content of the leaves from the growth chamber and field study is plotted as a function of  $\text{Al}^{3+}$  activity in Fig. 5. Mortality associated with Al toxicity occurred on soil 81 in the field study and

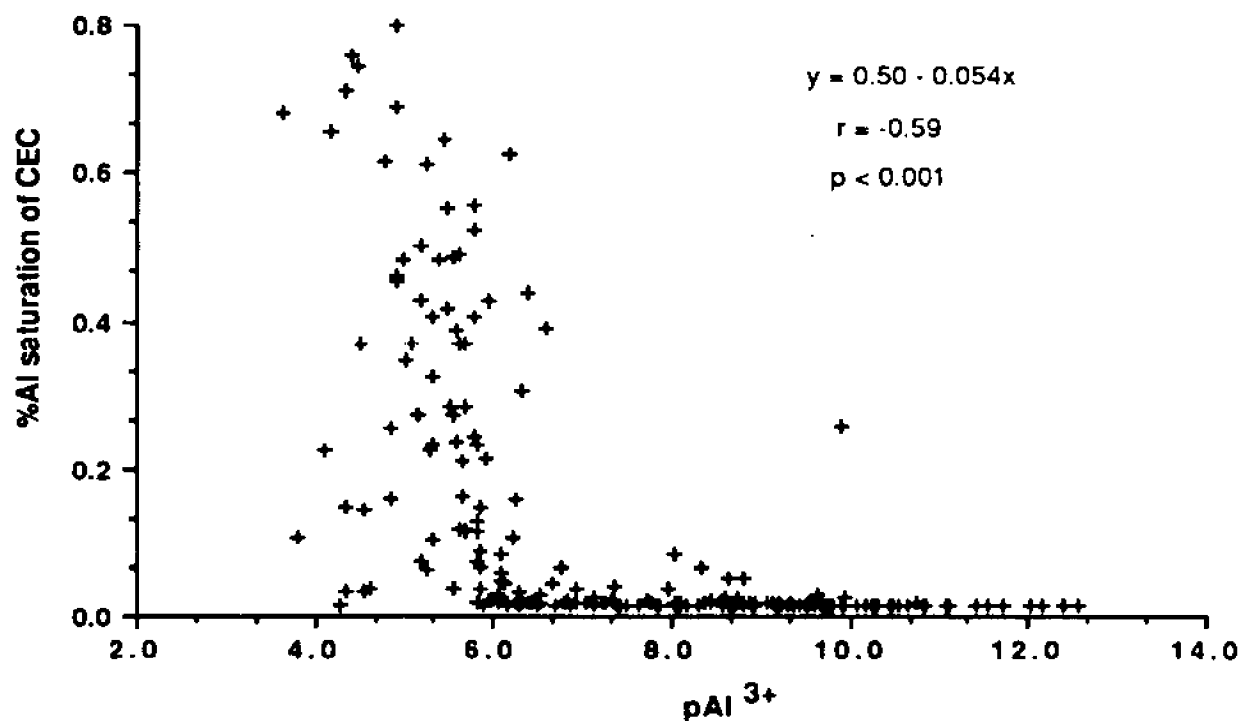


Fig. 4. The relationship between Al saturation of the CEC and  $Al^{3+}$  activity in the growth chamber and field studies ( $n = 233$ ).

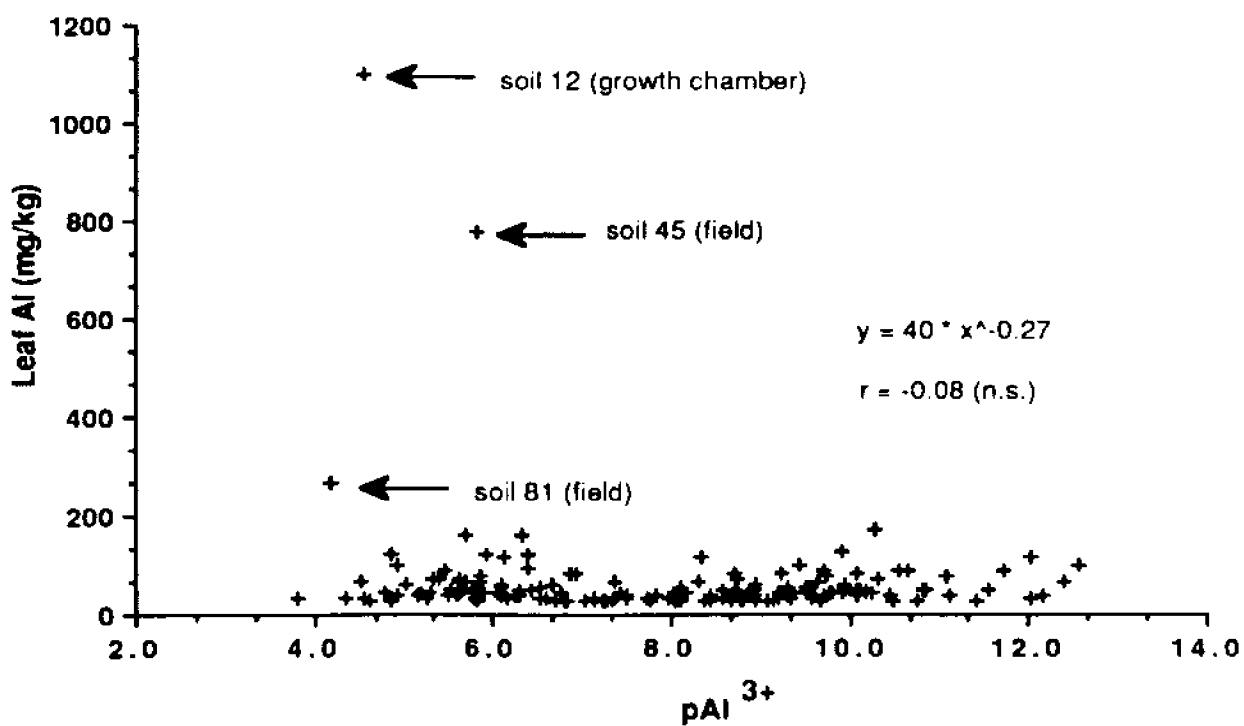


Fig. 5. The relationship between leaf Al and  $Al^{3+}$  activity in the growth chamber and field studies ( $n = 175$ ).



on soil 12 in the growth chamber study. The leaves of the plants at site 81 had an orange tinge to them and angled downward as if they had been broken at the node. Death of the plants grown on soil 12 in the growth chamber study occurred shortly after transplanting. The symptoms observed on soil 12 were chlorosis of the whole plant and a general lack of turgor. Three days after transplanting the tissue turned brown. Although the tissue Al concentration was over  $700 \text{ mg kg}^{-1}$  in the leaves of the plants growing on soil 45 in the field study, they appeared to be surviving. However, the stand was very sparse and the plants were stunted and somewhat yellow. Thawornwong and Van Diest (1974) and Tanaka and Naversero (1966) concluded that leaf Al contents are not useful indicators of Al toxicity.

Leaf P is plotted as a function of  $\text{pAl}^{3+}$  in Fig. 6. These data indicate that Al may be interfering with P uptake and/or assimilation. Tanaka and Naversero (1966) suggested that the mechanism of Al toxicity in rice is interference in P uptake and/or assimilation. They also observed decreases in leaf P as the Al level in solution was increased. Although leaf Al contents did not always increase with added Al in their hydroponic study, root Al levels did. They found much higher Al concentrations in the root and stated that it appeared to be associated with P. They concluded that the critical level of Al in solution for Al toxicity was dependent on the P status of the plant.

One possible mechanism in which Al can regulate the solubility of P in these soils would be the precipitation of variscite ( $\text{AlPO}_4$ ). The IAP of variscite is plotted as a function of pH in Fig. 7. This figure shows that most of the soils in this study were supersaturated with respect to variscite, indicating that precipitation of this compound

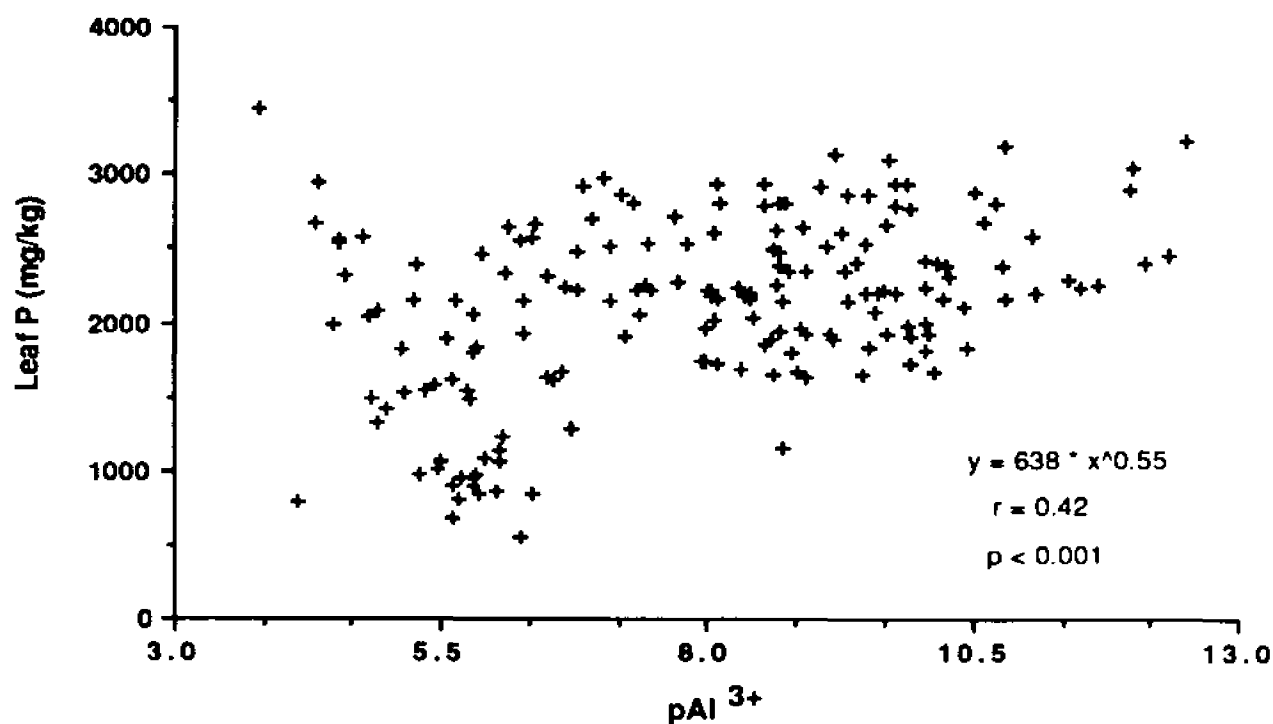


Fig. 6. The relationship between leaf P and Al<sup>3+</sup> activity in the growth chamber and field studies (n = 175).

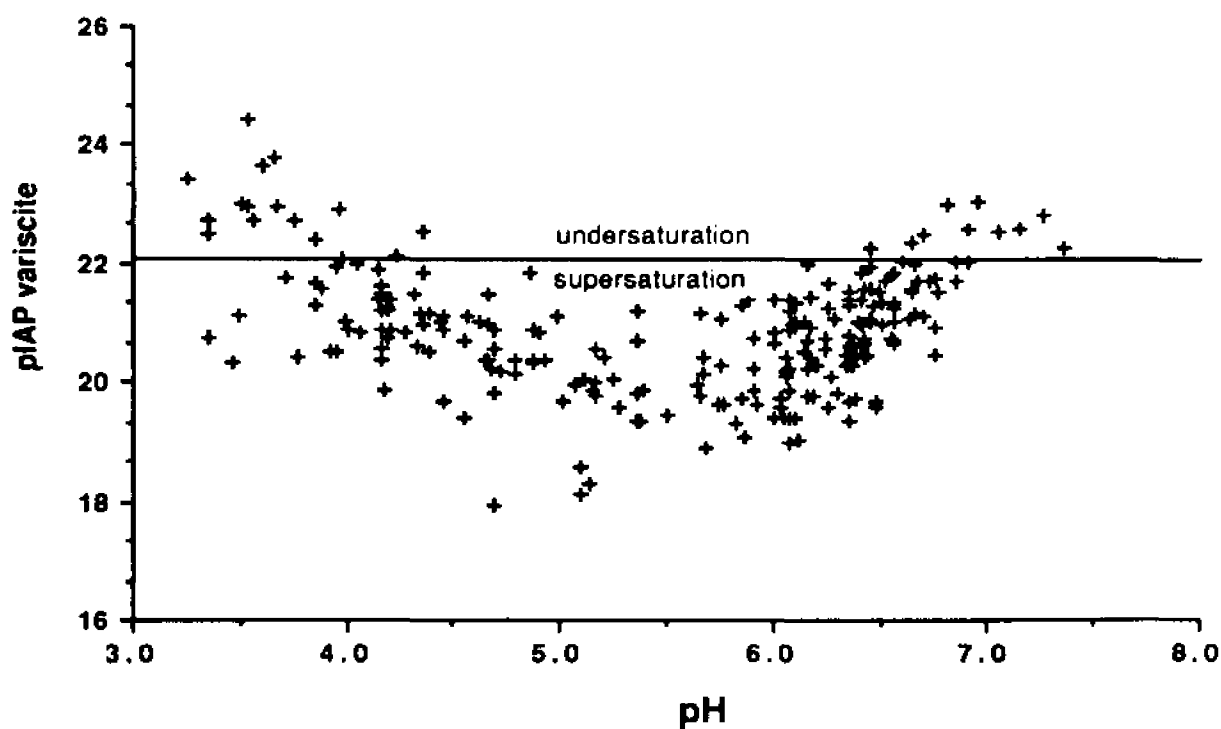


Fig. 7. The relationship between the pIAP of variscite and pH in the growth chamber and field studies (n = 234).

could be occurring. Although variscite may be controlling levels of P in solution, it is an unlikely candidate for the control of Al since there is far more Al in these soils than P.

#### CONCLUSIONS

Activities of  $\text{Al}^{3+}$  in flooded acid sulfate soils were found to be negatively correlated to pH. The mineral phases believed to be governing  $\text{Al}^{3+}$  activities were jurbanite under low pH conditions and amorphous  $\text{Al}(\text{OH})_3$  at high pH. Large quantities of exchangeable Al were observed and appeared to be in equilibrium with that in solution. It was hypothesized that solution  $\text{Al}^{3+}$  in these soils is not only controlled by precipitation/dissolution reactions, but adsorption/desorption as well.

Mortality of rice associated with Al toxicity was observed under field and growth chamber conditions. Although  $\text{Al}^{3+}$  activities were not correlated with leaf Al contents, they were found to be negatively correlated to leaf P contents. This phenomenon was believed to be due to P precipitation by Al, as most of the soils studied were strongly supersaturated with respect to variscite.

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## Chapter Six

### Boron, Copper, Molybdenum and Zinc Availability and Uptake by Rice in Acid Sulfate Soils

## ABSTRACT

Metal availability and uptake by rice were evaluated in 134 flooded acid sulfate soils in the Central Plains region of Thailand and in a growth chamber experiment utilizing 50 of the same soils. Soil and plant metal analyses were conducted at the panicle differentiation stage of growth in both studies and in the soil prior to planting in the growth chamber study. Metal activities in soil solutions were determined from free metal concentrations using GEOCHEM and activity coefficients using the Davies equation.

The results of this study indicated that  $\text{Zn}^{2+}$  activities were negatively correlated with pH and may be controlled by franklinite in these soils. Activities of  $\text{Cu}^{2+}$  were found to be highly correlated to pe. The suspected stable solid phase of Cu in these soils was cuprous ferrite. Activities of  $\text{MoO}_4^{2-}$  were positively correlated to pH and appeared to be controlled by wulfenite. Activities of  $\text{B(OH)}_4^-$  and  $\text{B(OH)}_3^0$  were found to be highly correlated to pH and ionic strength, respectively, with the latter being the dominant B ion found in these soils.

Leaf metal analyses indicated that leaf Cu contents were positively correlated with  $\text{Cu}^{2+}$  activity and pe. Leaf Mo contents were found to be positively correlated with  $\text{MoO}_4^{2-}$  activity and pH. Leaf Zn contents were not significantly correlated to  $\text{Zn}^{2+}$  activities, but were found to be negatively correlated to  $\text{CO}_3^{2-}$  activities.

Key words - Cuprous ferrite, flooded soils, franklinite, GEOCHEM, islemanite, metal activity, mineral equilibria, trace metals, wulfenite.

Molybdenum forms many complexes and polymerized species; however, in solutions with less than  $10^{-4}$  M Mo, the polymeric forms are not of great importance (Jenkins and Wain, 1963). The solution species of Mo that are generally found in soils are  $\text{MoO}_4^{2-}$ ,  $\text{HMoO}_4^-$ , and  $\text{H}_2\text{MoO}_4^0$  (Chojnacki and Oleksyn, 1963).

Very little research has been conducted on the phases responsible for controlling solution Mo levels. Titley (1963) suggested that  $\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$  may be important in acid soils. Iron oxides have also been implicated in controlling Mo availability (Reyes and Jurinak, 1967; Jenne, 1979). Vlek and Lindsay (1977) showed that one Colorado soil (out of 13 studied) was in equilibrium with  $\text{PbMoO}_4$  (wulfenite). They concluded that the solubility of Mo in the other soils was controlled by specific adsorption. Kaback and Runnells (1980) stated that Mo in the sediment of Tenmile Creek in Colorado was chiefly adsorbed on coatings of iron oxyhydroxide. They found that the stream water was undersaturated with respect to ferrimolybdate, molybdenite, powellite and ilsemanite and concluded that adsorption of Mo by iron oxyhydroxides was the most important process in regulating soluble Mo. Under acidic, reducing conditions such as that found in acid bogs and mangrove soils, ilsemanite ( $\text{Mo}_3\text{O}_8$ ) is expected to be the stable solid phase of Mo (Vlek and Lindsay, 1977).

Lindsay (1972) stated that very little is known about B minerals in soils since most work has focused on its adsorption by hydrous oxides of Fe and Al and interlayer alumino-silicates. He also indicated that there is no basis for concluding that B solubility in soils is determined by solid phase B minerals.

Flooding has often been shown to decrease the solubility of Zn in soils (Forno et al, 1975; Iu et al., 1981; Van Breemen et al., 1980). Yoon et al. (1975) found that changes in water soluble Zn concentrations with time in a flooded rice soil were negatively correlated with the bicarbonate concentration and pH. They suggested that this may have been due to the formation of zinc carbonate and/or hydroxide. Kittrick (1976) reported that sphareelite ( $\text{ZnS}$ ) was the most stable solid phase of Zn in flooded soils. Gilmour and Kittrick (1979) calculated that  $\text{ZnS}$  was the only possible solid phase which could be controlling solution Zn activities in flooded soils assuming the  $\text{H}_2\text{S}$  (g) pressure in solution was similar to that in the atmosphere [ $\text{pH}_2\text{S}(\text{g})=10.3$ ] and that between 50 to 90% of solution Zn was complexed by organics. In situations where  $\text{H}_2\text{S}$  levels were lower than this, they predicted  $\text{Zn}_2\text{SiO}_4$  or  $\text{ZnCO}_3$  would be likely candidates for solubility control. Lindsay (1979) and Saiwan and Lindsay (1986) speculated that  $\text{ZnFe}_2\text{O}_4$  (franklinite) may be the most stable Zn mineral in flooded soils.

Like Fe and Mn, Cu is a redox element and is transformed from  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  under reducing conditions. However, very little research has been conducted on the solid phases of Cu in flooded soils. Lindsay (1979) calculated that above  $\text{pe} + \text{pH}$  of 14.89, Cu solubility is controlled by soil Cu and is dependant on pH only. He also predicted that between  $\text{pe} + \text{pH}$  of 4.73 and 14.89, Cu solubility is controlled by  $\text{Cu}_2\text{Fe}_2\text{O}_4$  (cuprous ferrite). Below  $\text{pe} + \text{pH}$  of 4.73 he indicated that  $\text{Cu}_2\text{S}$  (chalcocite) would be the solid phase of Cu governing solution activities. However, to date no attempts to elucidate the stable mineral phases of Cu in flooded soils have been reported in the literature.



Studies on micronutrient uptake by rice have usually indicated that uptake is related to the concentration or the activity of a particular species in soil solution. For example, Gilmour (1977) found that leaf Cu and Mn were positively correlated to soil solution Cu and Mn concentrations. Similarly, Yoon et al. (1975) found Y-leaf Zn contents were positively correlated with Zn in soil solution. Schwab and Lindsay (1983) found that Mn uptake was related to  $Mn^{2+}$  activity.

The objectives of this study were (1) to measure the availability of B, Cu, Mo, and Zn in flooded acid sulfate soils cropped to rice, (2) to determine what factors influence the availability of these micronutrients in these soils, (3) to determine the stable solid phases of these elements in these soils, and (4) to elucidate the relationships between availability of these metals and uptake by rice.

#### METHODS AND MATERIALS

The results reported in this chapter were obtained from a field study conducted on 134 flooded acid sulfate soils in the Central Plains region of Thailand and from a growth chamber study on 50 of the same soils. Metal availability and uptake by rice were evaluated at the panicle differentiation stage of growth. The methods used in this study are given elsewhere (chapter two).

## RESULTS AND DISCUSSION

The negative log of  $\text{Zn}^{2+}$  activity ( $\text{pZn}^{2+}$ ) is plotted as a function of pH in Fig. 1. These data show that  $\text{Zn}^{2+}$  activities were negatively correlated with pH.  $\text{Zn}^{2+}$  activities were positively correlated to pe and pe + pH.  $\text{Zn}^{2+}$  activities were also positively correlated with  $\text{SO}_4^{2-}$  activity and negatively correlated with  $\text{CO}_3^{2-}$  and  $\text{PO}_4^{3-}$  activity (Table 1). Similar results were found by Yoon et al. (1975) who observed that changes in solution Zn were negatively correlated with pH and bicarbonate concentrations.

Lindsay (1979) indicated that the most likely mineral accounting for Zn solubility in soils is franklinite. In order to determine if Zn solubility could be governed by this mineral in acid sulfate soils, the IAP of  $\text{ZnFe}_2\text{O}_4$  was plotted as a function of pH as shown in Fig. 2. The solid line in this figure represents franklinite equilibria. The data in this figure indicate that many of the soils investigated in this study were supersaturated with respect to franklinite. Therefore, this mineral phase is a possible candidate for governing the solubility of  $\text{Zn}^{2+}$  in acid sulfate soils.

$\text{Zn}^{2+}$  activity is probably not controlled by  $\text{Zn}_3(\text{PO}_4)_2$  (hopeite) as the maximum pIAP ( $-\log$  ion activity product) of this mineral was 41.65 (Table 2) which is considerably smaller than the reported pK of 35.3. Castro (1977) reported similar results for acid sulfate soils from the Philippines and Vietnam. Equilibria calculations also indicated that these soils were undersaturated with respect to  $\text{ZnCO}_3$  (smithsonite) and  $\text{Zn}_2\text{SiO}_4$  (willenite). This agrees with the findings of Gilmour and Kittrick (1979) who showed that a typical Arkansas rice soil was undersaturated with respect to willemite, smithsonite, and hopeite.

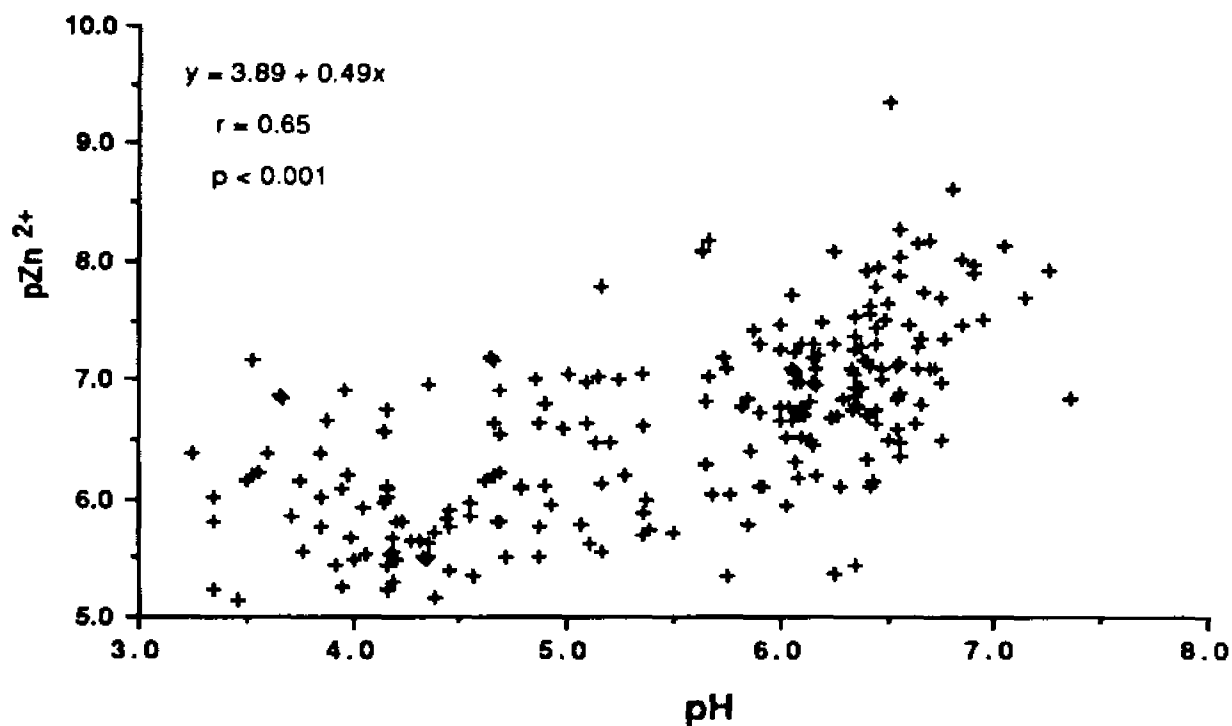


Fig. 1. The relationship between  $Zn^{2+}$  activity and pH in the growth chamber and field studies (n = 234).

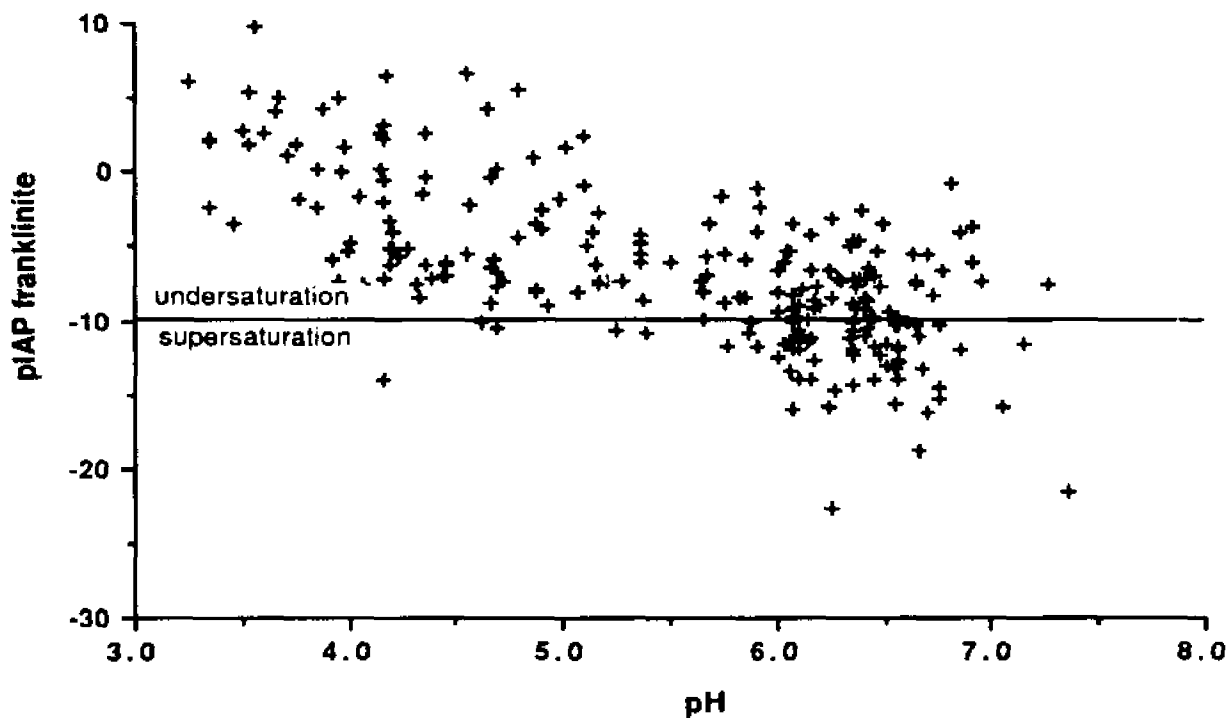


Fig. 2. The relationship between the pIAP of franklinite and pH in the growth chamber and field studies (n = 234).

Table 1 - Significant simple correlation coefficients (.05 level) between trace metal activities† and Y-leaf metal concentrations‡ and soil physico-chemical parameters.

variable	pH	pe	pe + pH	pSO <sub>4</sub> <sup>2-</sup>	pCO <sub>3</sub> <sup>2-</sup>	pPO <sub>4</sub> <sup>3-</sup>	I.S.
pB(OH) <sub>4</sub> <sup>-</sup>	-.94	.67	.42	-.40	-.92	.95	ns
pB(OH) <sub>3</sub> <sup>0</sup>	.16	-.15	ns	.39	ns	ns	-.66
pMoO <sub>4</sub> <sup>2-</sup>	-.38	.34	.25	ns	.36	.46	-.31
pZn <sup>2+</sup>	.65	-.59	-.45	.53	-.66	-.60	-.31
pCu <sup>2+</sup>	.61	-.83	-.79	.41	-.63	-.60	ns
leaf Zn	ns	ns	ns	ns	.20	ns	ns
leaf Cu	-.33	.48	.43	-.49	.37	.32	.44
leaf Mo	.17	-.18	ns	.17	ns	-.21	ns

† n = 234 for metal activities and soil parameters

‡ n = 175 for leaf concentrations

Table 2 - Ion activity products and equilibrium constants of Cu, Mo and Zn minerals.

Reaction	pIAPmax*	pK	reference
$\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O} = 3\text{Zn}^{2+} + 2\text{PO}_4^{3-} + 4\text{H}_2\text{O}$	38.89	35.30	1
$\text{ZnCO}_3 = \text{Zn}^{2+} + \text{CO}_3^{2-}$	11.78	10.24	1
$\text{Zn}_2\text{SiO}_4 + 4\text{H}^+ = 2\text{Zn}^{2+} + \text{H}_4\text{SiO}_4^0$	-12.97	-13.15	1
$\text{ZnO} + 2\text{H}^+ = \text{Zn}^{2+} + \text{H}_2\text{O}$	-7.85	-11.16	1
$\text{CuO} + 2\text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{O}$	-5.86	-7.66	1
$\text{Cu}_2(\text{OH})_2\text{CO}_3 + 2\text{H}^+ = 2\text{Cu}^{2+} + \text{CO}_3^{2-} + 2\text{H}_2\text{O}$	7.83	5.16	1
$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2 + 2\text{H}^+ = 3\text{Cu}^{2+} + 2\text{CO}_3^{2-} + 2\text{H}_2\text{O}$	21.35	16.73	1
$\text{MoO}_3 + \text{H}_2\text{O} = \text{MoO}_4^{2-} + 2\text{H}^+$	13.20	12.10	2
$\text{FeMoO}_4 = \text{Fe}^{2+} + \text{MoO}_4^{2-}$	9.33	7.70	1
$\text{Fe}_2(\text{MoO}_4)_3 = 2\text{Fe}^{3+} + 3\text{MoO}_4^{2-}$	34.39	38.82	2
$\text{CaMoO}_4 = \text{Ca}^{2+} + \text{MoO}_4^{2-}$	9.13	7.94	1
$\text{MnMoO}_4 = \text{Mn}^{2+} + \text{MoO}_4^{2-}$	10.15	4.13	1
$\text{ZnMoO}_4 = \text{Zn}^{2+} + \text{MoO}_4^{2-}$	11.75	4.94	1

1 - Lindsay (1979)

2- Vlek and Lindsay (1977)

\* - negative log of ionic activity product (maximum observed)

However, they predicted that ZnS was the controlling mineral phase in the soil they studied. Control of Zn, Cu, and Mo by sulfides could not be evaluated in this study since free sulfide concentrations were always below the detection limit of the  $S^{2-}$  electrode used ( $10^{-7}$  M).

Gilmour and Kittrick (1979) were also unable to measure  $S^{2-}$  activities and assumed the  $pH_2S(g)$  was 10.3, a value which represents equilibrium with the atmosphere. Since sulfide levels of this magnitude were entirely possible in this study, control of Zn by sulfides cannot be ruled out.

Although adsorption reactions may also play an important role in governing Cu and Zn solubility, it was not possible to determine exchangeable Cu and Zn due to contamination in the sodium acetate used to extract exchangeable metals. Even though Cu and Zn contamination of the extractant was slight, the blanks occasionally had higher levels of Zn and invariably had higher levels of Cu than the soil extracts. Cu levels in the sodium acetate extracts from the soils were so low (less than that in distilled, deionized water) that it appeared as if Cu precipitation and/or specific adsorption reactions may have occurred during the extraction process.

The negative log of the  $Cu^{2+}$  activity is plotted as a function of  $pe$  in Fig. 3. These data demonstrate the effect of reduction on the activity of  $Cu^{2+}$  in flooded soils. Above  $pe$  2.6,  $Cu^{2+}$  is the dominant form of Cu present and below  $pe$  2.6,  $Cu^+$  is the dominant form.

Equilibria calculations indicated that the soils investigated in this study were undersaturated with respect to CuO (tenorite),  $Cu_2(OH)_2CO_3$  (malachite) and  $Cu_3(OH)_2(CO_3)_2$  (azurite), (Table 2). In

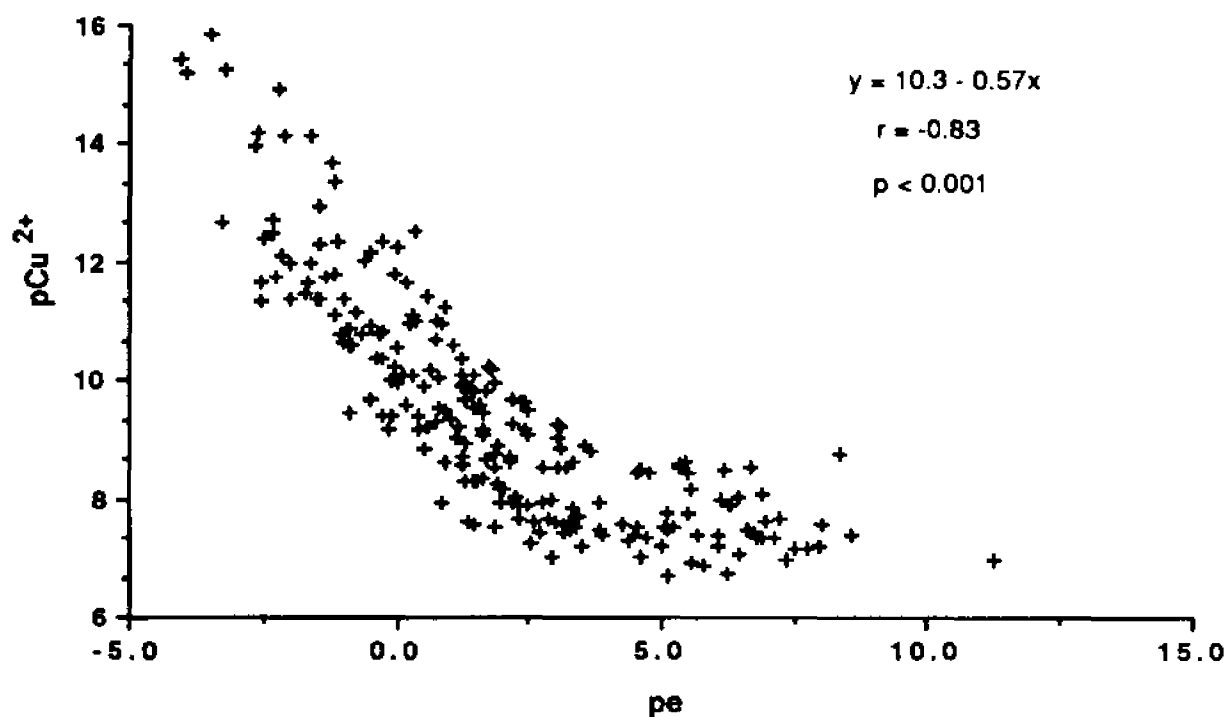


Fig. 3. The relationship between  $Cu^{2+}$  activity and  $pe$  in the growth chamber and field studies ( $n = 234$ ).

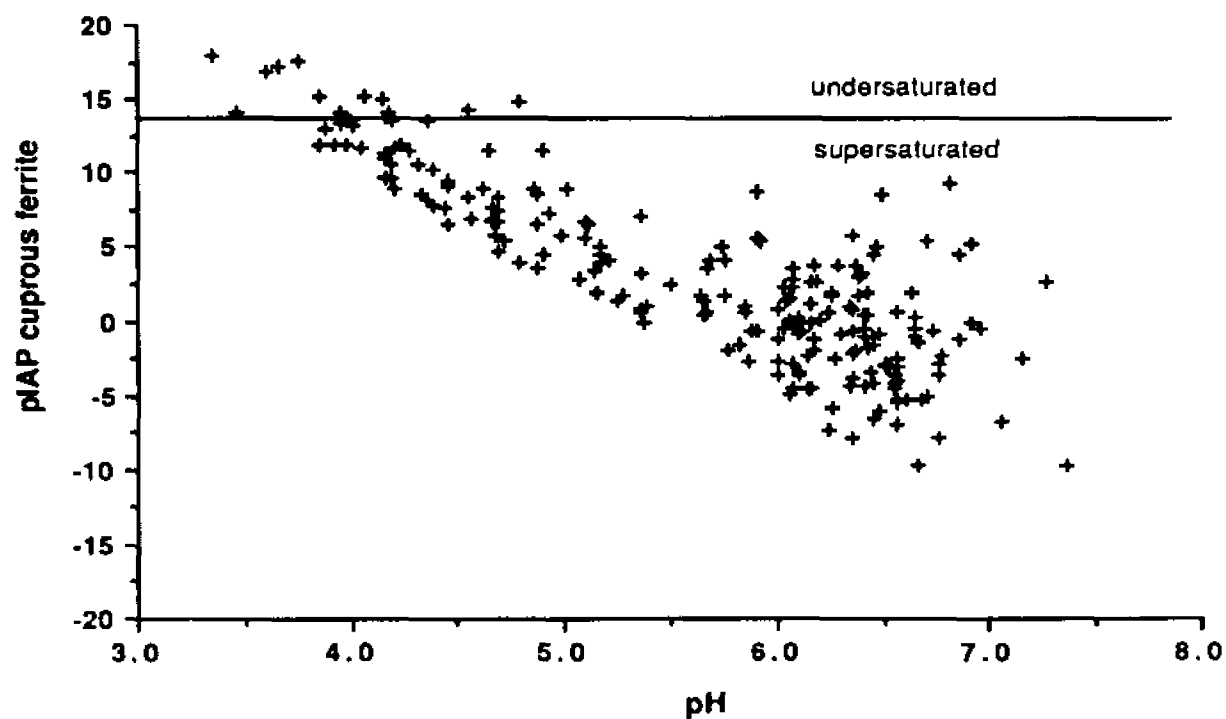


Fig. 4. The relationship between  $pIAP$  of cuprous ferrite and  $pH$  in the growth chamber and field studies ( $n = 234$ ).

order to determine if cuprous ferrite was a possible stable phase of Cu, the IAP of  $\text{Cu}_2\text{Fe}_2\text{O}_4$  was plotted as a function of pH as shown in Fig. 4. The solid line in this figure represents equilibrium conditions with respect to cuprous ferrite. These data show that many of the soils studied were strongly supersaturated with respect to cuprous ferrite, indicating that it may be the solid phase controlling Cu solubility in acid sulfate soils. These data support the postulations set forth by Lindsay (1979), who calculated that cuprous ferrite would be the most stable solid phase of Cu under a wide range of redox conditions in flooded soils. Another possible mineral phase which may be important in governing Cu solubility in acid sulfate soils is chalcocite. However, as stated earlier sulfide mineral formation could not be evaluated in this study.

The negative log of the  $\text{MoO}_4^{2-}$  activity is plotted as a function of pH in Fig. 5. These data indicate that  $\text{MoO}_4^{2-}$  activity was positively correlated with pH. Ponnampetuma (1972) indicated that the increase in water soluble Mo in acid soils following flooding was due to increases in pH. The data shown in this figure would appear to support that hypothesis.  $\text{MoO}_4^{2-}$  activity was also shown to be negatively correlated to pe and pe + pH (Table 1).

Equilibria calculations indicated that the soils investigated in this study were undersaturated with respect to ferrous molybdate, ferric molybdate, calcium molybdate, manganous molybdate, and zinc molybdate (Table 2). In order to determine if wulfenite and/or ilsemanite were controlling  $\text{MoO}_4^{2-}$  activities in these soils, the IAP's of these minerals were plotted as a function of pH as shown in Fig. 6. These data indicate that under low pH conditions, several of the soils were



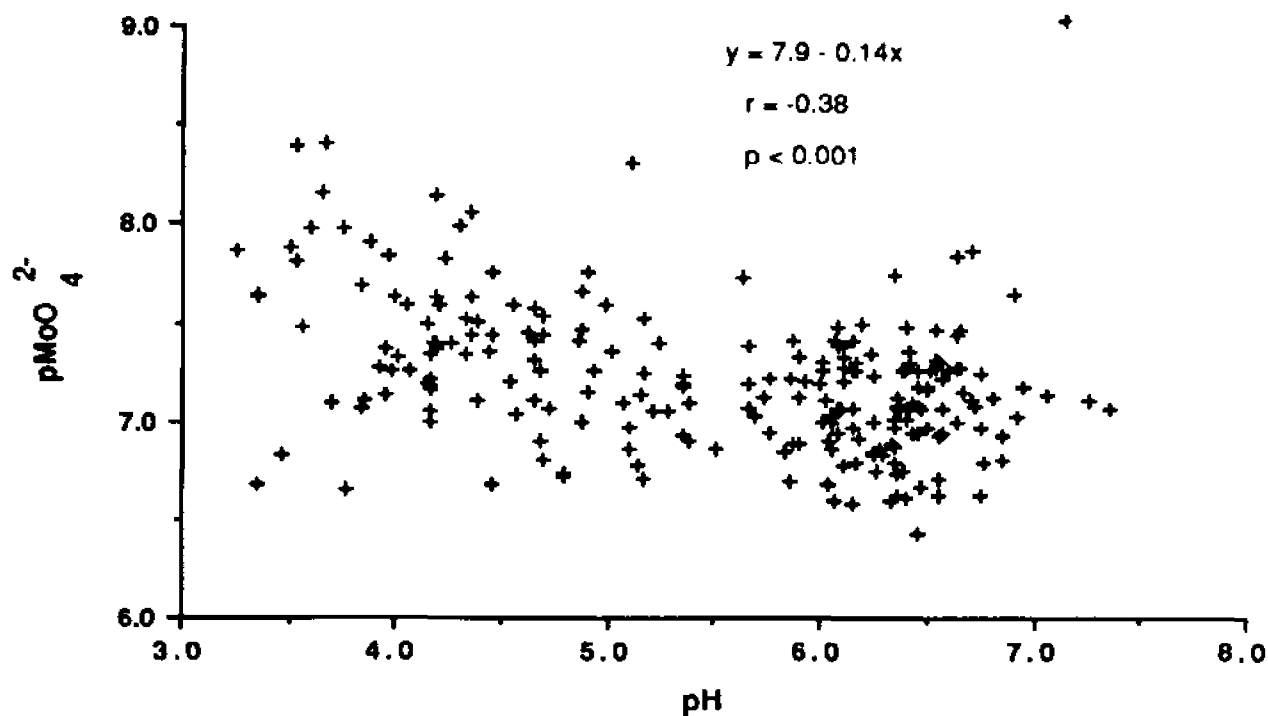


Fig. 5. The relationship between  $\text{MoO}_4^{2-}$  activity and pH in the growth chamber and field studies ( $n = 234$ ).

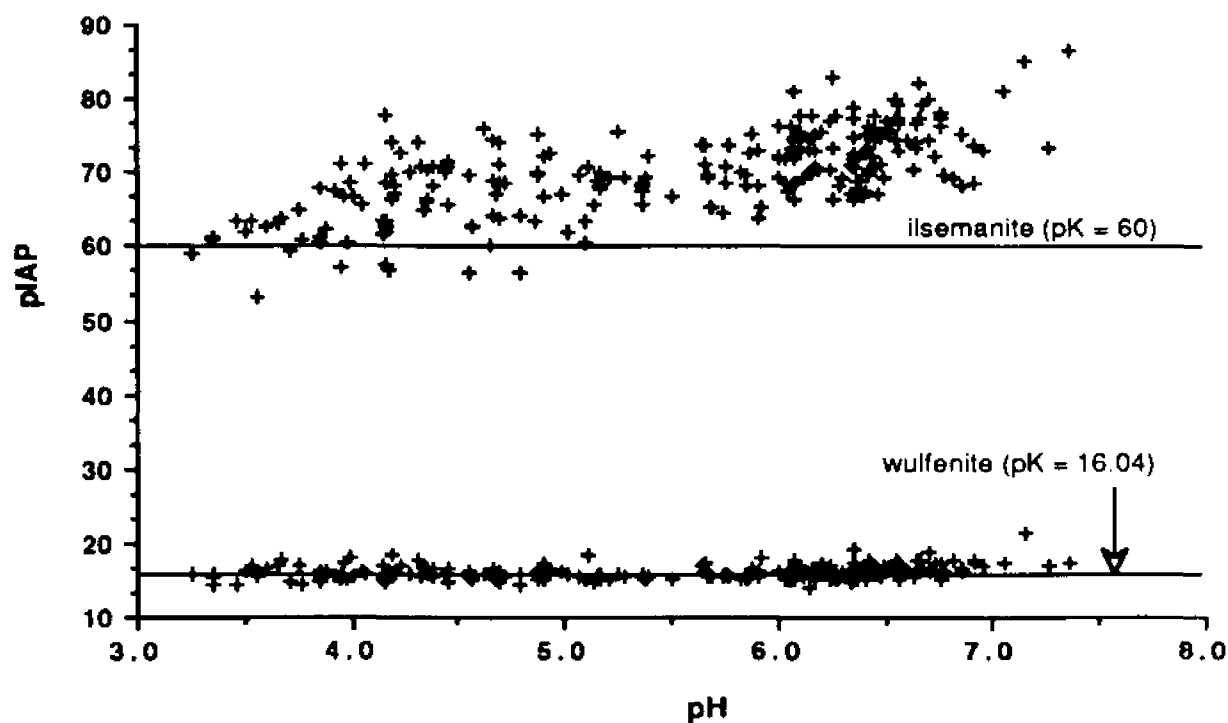


Fig. 6. The relationship between the ion activity products of ilsemanite and wulfenite and pH in the growth chamber and field studies ( $n = 234$ ).

supersaturated with respect to ilsemanite. Vlek and Lindsay (1977) stated that ilsamanite may be the stable phase of Mo in very acid soils. However, Fig. 6 demonstrates that wulfenite would be expected to be the stable Mo mineral under most conditions in these soils. Although  $\text{MoS}_2$  (molybdenite) may also be a possible candidate for Mo control in these soils, sulfide equilibria could not be evaluated as stated earlier.

The negative log of  $\text{B(OH)}_4^-$  is plotted as a function of pH in Fig. 7. These data demonstrate the strong pH dependence of this chemical moiety. However, most of the B in solution in these soils is in the form of  $\text{B(OH)}_3^0$ . This species of B was found to be highly correlated with ionic strength as shown in Fig. 8. This trend probably reflects the marine origins of B in these soils. The highest  $\text{B(OH)}_3^0$  activity was found at a farmer's field located near the Bang Pakong rice research station, within 1 km of the Gulf of Siam. Equilibria calculations based upon the thermodynamic data of Bassett (1976) indicated that all of the soils studied in this investigation were strongly undersaturated with respect to B minerals (data not shown). These observations support the statement made by Lindsay (1972) who indicated that B solubility in soils is not controlled by mineral equilibria.

#### NUTRIENT UPTAKE

Leaf Cu concentrations are plotted as a function of  $\text{pCu}^{2+}$  in Fig. 9. These data indicate that leaf Cu contents were significantly correlated with  $\text{pCu}^{2+}$ . Gilmour (1977) showed a positive correlation between soil solution Cu and leaf Cu in a typical rice soil of Arkansas. Leaf Cu concentrations were negatively correlated with pH and  $\text{CO}_3^{2-}$

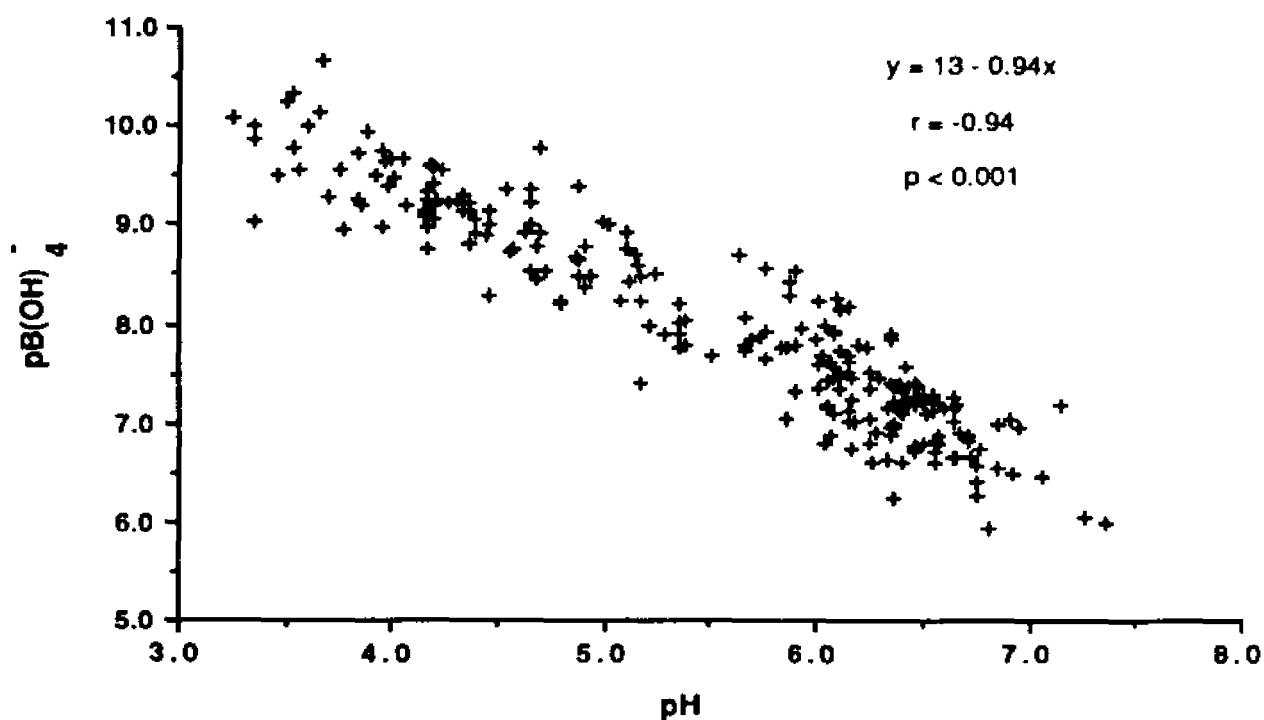


Fig. 7. The relationship between  $B(OH)_4^-$  activity and pH in the growth chamber and field studies ( $n = 234$ ).

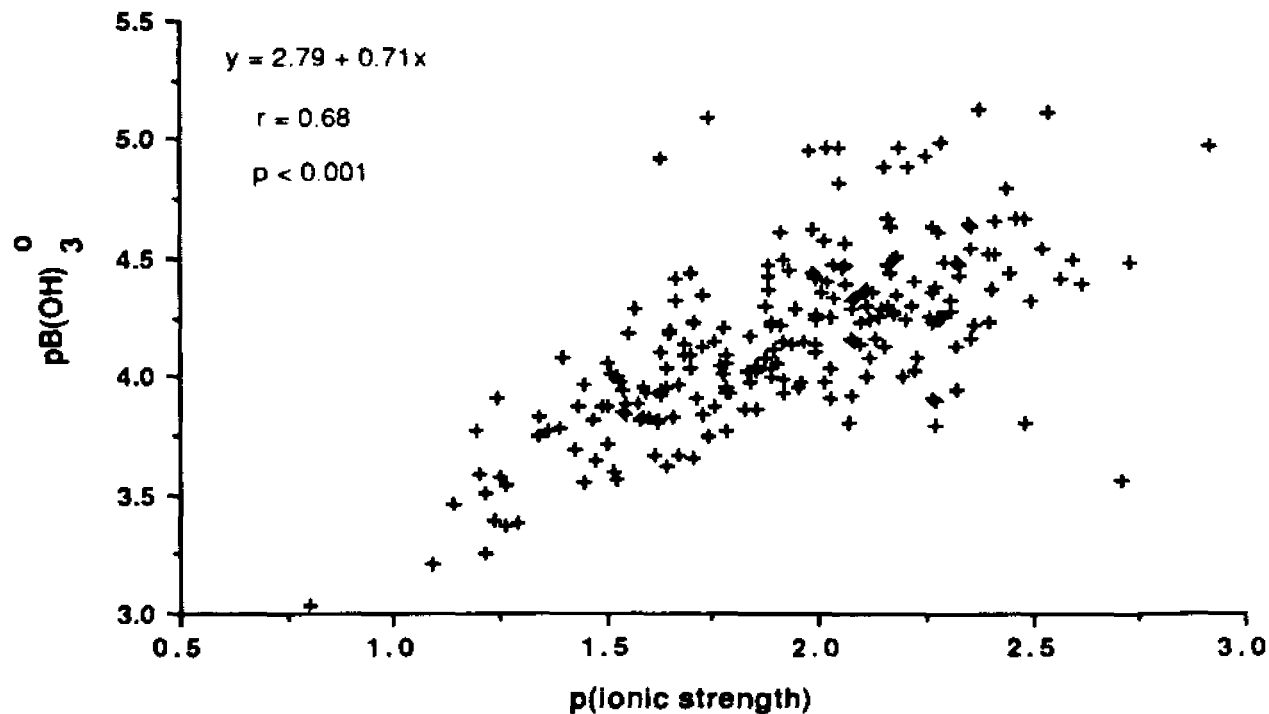


Fig. 8. The relationship between  $B(OH)_3^0$  activity and ionic strength in the growth chamber and field studies ( $n = 234$ ).

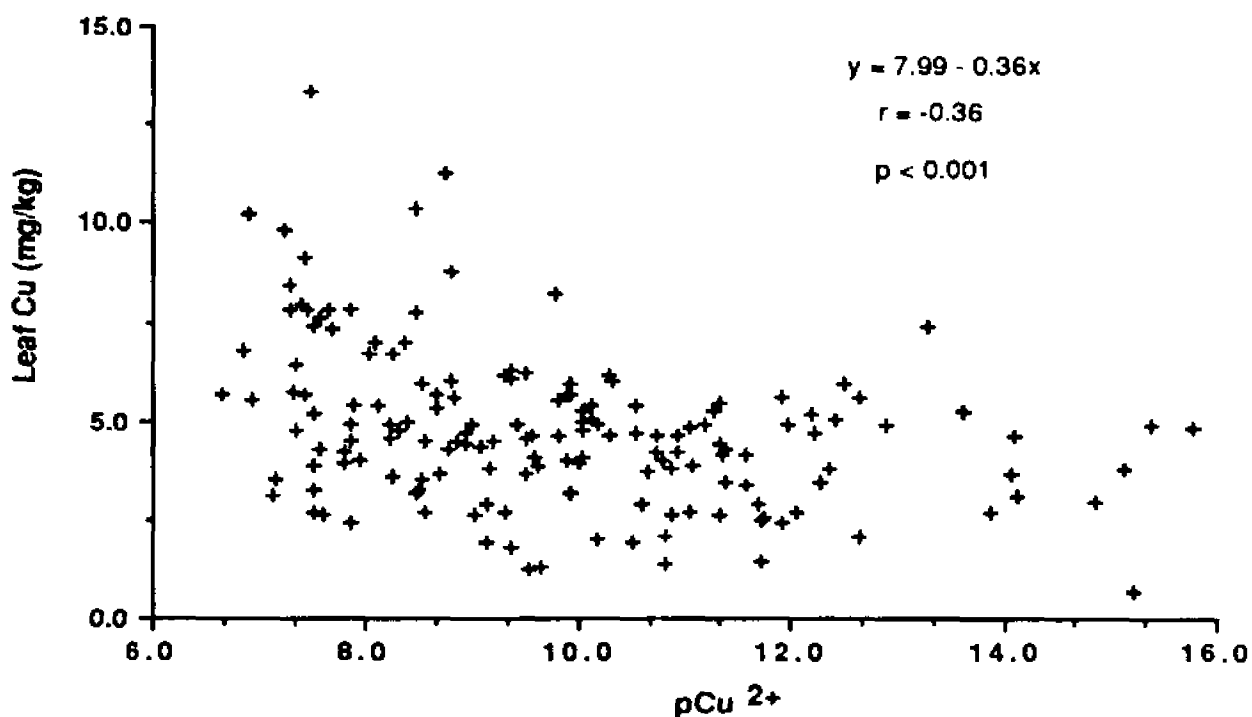


Fig. 9. The relationship between leaf Cu and  $Cu^{2+}$  activity in the growth chamber and field studies ( $n = 175$ ).

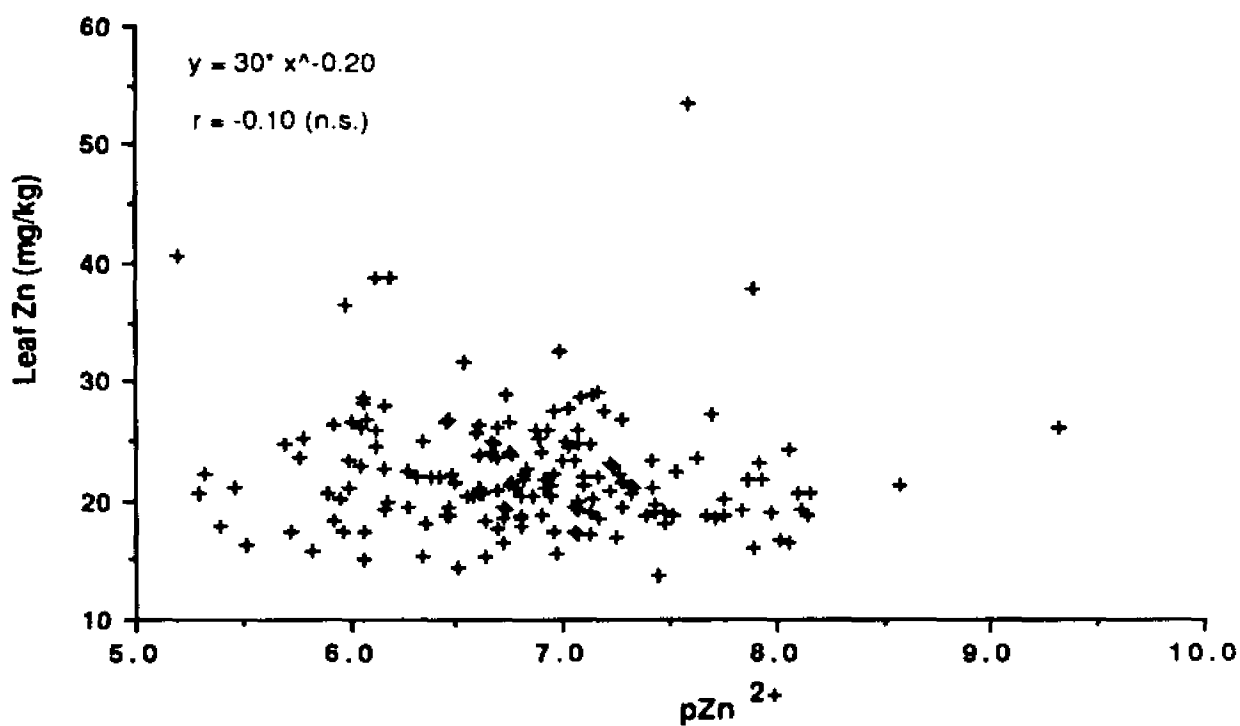


Fig. 10. The relationship between leaf Zn and  $Zn^{2+}$  activity in the growth chamber and field studies ( $n = 175$ ).

activities and positively correlated with  $p_e$ ,  $p_e + pH$  and  $SO_4^{2-}$  activities (Table 1).

The average leaf Cu content was  $4.6 \mu g g^{-1}$ . This is comparable to that reported for rice leaves around midseason (Gilmour, 1977). The lowest leaf Cu content ( $0.5 \mu g g^{-1}$ ) was observed on a field sample which had one of the highest pH's observed (7.2). The soil was very dark at this site and appeared to be high in organic matter, thus comprising conditions for Cu deficiency to occur. However, since the stand appeared very vigorous and the yield of this field (3 metric tons  $ha^{-1}$ ) was above the national average (1.9 metric tons  $ha^{-1}$ ), Cu deficiency was not suspected. Tanaka and Yoshida (1970) reported the critical Cu concentration in rice straw at maturity for deficiency and toxicity was 6 and 30  $mg kg^{-1}$ , respectively. Due to the differences in plant parts sampled and plant age, direct comparisons of the results of this study with the values presented by Tanaka and Yoshida (1970) may not be valid. However, Cu toxicity was not believed to be a problem on these soils since the highest Cu content observed was 13  $mg kg^{-1}$ .

Leaf Zn concentrations are plotted as a function of  $pZn^{2+}$  in Fig. 10. As these data indicate, leaf Zn was not correlated with  $Zn^{2+}$  activity. Although leaf Zn was significantly correlated with  $p_e$  and  $pCO_3^{2-}$ , the relationships were not well defined (Table 1). Leaf Zn was not significantly correlated with pH or  $p_e + pH$ . The reason for the independence of leaf Zn concentrations from soil physico-chemical parameters in this study is not understood.

The average leaf Zn content was 21.4  $mg kg^{-1}$ . This value is in the range of that reported by Gilmour (1977) for rice leaves at midseason. The minimum and maximum Zn contents were 12.8 and 52.7  $mg kg^{-1}$ ,

respectively. Tanaka and Yoshida (1970) reported that 10 and 1500 mg kg<sup>-1</sup> were the critical Zn levels in rice for deficiency and toxicity, respectively.

Leaf Mo is plotted as a function of  $\text{pMoO}_4^{2-}$  in Figure 11. These data indicate that leaf Mo was significantly correlated with  $\text{pMoO}_4^{2-}$ . Leaf Mo was positively correlated with pH and negatively correlated with pe, but not significantly correlated to pe + pH (Table 1). The average leaf Mo concentration was 1.4 mg kg<sup>-1</sup>. The minimum and maximum leaf Mo concentrations were .22 and 7.2 mg kg<sup>-1</sup>, respectively. The critical Mo concentrations in the rice plant for toxicity and deficiency have not been defined.

Leaf B contents could not be evaluated due to B contamination from the glassware used to digest the samples. The author suggests that workers interested in leaf B utilize teflon containers for acid digestions of plant material.

## CONCLUSIONS

The results of this study indicate that  $\text{Zn}^{2+}$  activities were negatively correlated with pH and may be controlled by franklinite in these soils.  $\text{Cu}^{2+}$  activities were found to be highly correlated to pe. The suspected stable solid phase of Cu in these soils was cuprous ferrite.  $\text{MoO}_4^{2-}$  activities were positively correlated to pH and appeared to be controlled by wulfenite.  $\text{B(OH)}_4^-$  and  $\text{B(OH)}_3^0$  activities were found to be highly correlated to pH and ionic strength, respectively, with the latter being the dominant B ion found in these soils. The relationship between  $\text{B(OH)}_3^0$  activities and ionic strength is an indication that B in these soils is of marine origins.

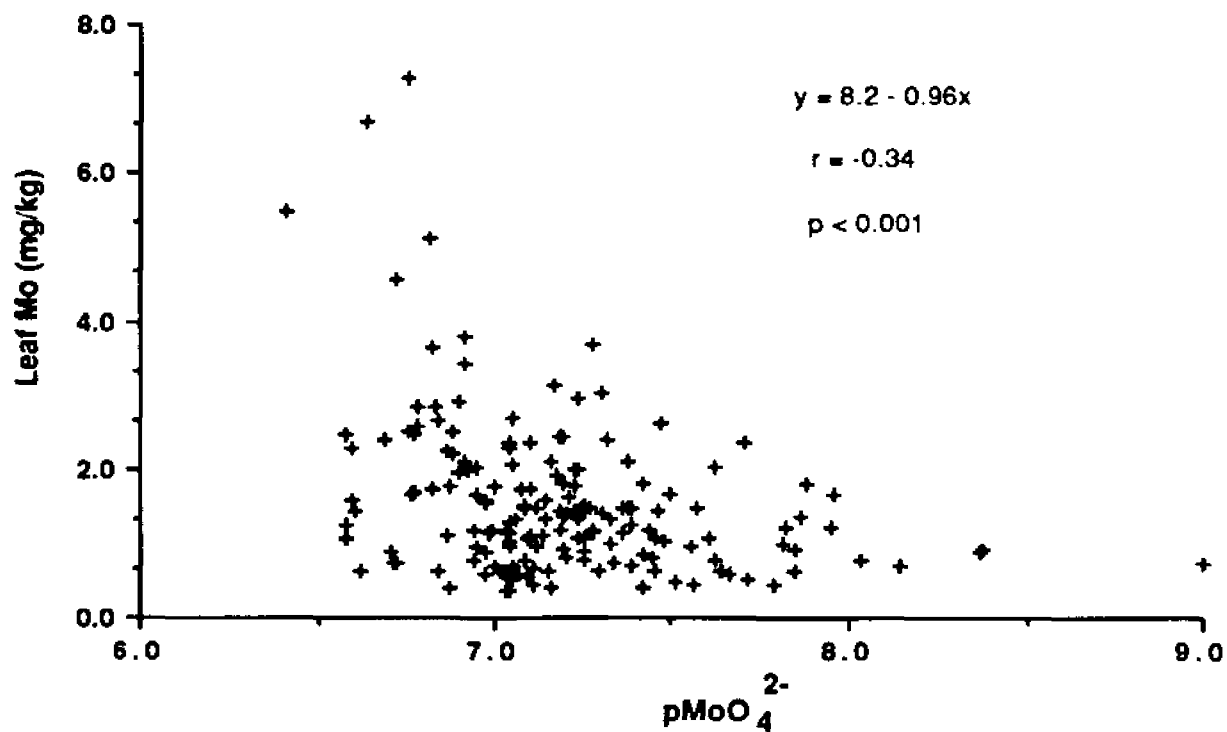


Fig. 11. The relationship between leaf Mo and  $\text{MoO}_4^{2-}$  activity in the growth chamber and field studies ( $n = 175$ ).

Leaf metal analyses indicated that leaf Cu contents were positively correlated with the activities of  $\text{Cu}^{2+}$ ,  $\text{SO}_4^{2-}$ , pe and ionic strength, whereas they were negatively correlated with the activities of  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$  and pH. Leaf Mo contents were found to positively correlated with the activities of  $\text{MoO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and pH and negatively correlated with pe and  $\text{SO}_4^{2-}$  activity. Leaf Zn contents were not significantly correlated to  $\text{Zn}^{2+}$  activities, but were found to be negatively correlated to  $\text{CO}_3^{2-}$  activities.



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## Chapter Seven

### Factors Affecting Rice Growth on Acid Sulfate Soils

## ABSTRACT

Metal availability and uptake by rice were evaluated in 134 flooded acid sulfate soils in the Central Plains of Thailand and in a growth chamber experiment utilizing 50 of the same soils. Measures of growth indices in these experiments were (1) dry matter production at panicle differentiation in the growth chamber study, and (2) rough rice yields from the previous year in the field study.

Simple linear correlations indicated that growth was positively correlated with the activities of  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{B(OH)}_4^-$ ,  $\text{Ca}^{2+}$ , pH, exchangeable Ca, exchangeable Mg and E'-Ca. Growth was found to be negatively correlated with the activities of  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , pe, % Al saturation of the CEC, E-Fe and E'-Fe. A micronutrient fertility trial also indicated that Si deficiencies may be occurring on limed acid sulfate soils.

Results from multiple correlation analysis indicated that E'-Fe, pH and ionic strength provided the best 3 variable model describing dry matter production in the growth chamber study. In the field study the best 2 variable model describing yields included pH and E'-Fe. In light of these findings, the most important constraints to rice growth on acid sulfate soils were believed to be (1) Fe stress - which is due to the combined effects of Fe as well as other divalent cations, and (2) acidity - which includes the combined effects of pH, Al stress and P deficiency.

Key words - Fe toxicity, Al toxicity, Ca deficiency, P deficiency, flooded soils, metal toxicity, Oryza sativa, metal activities.

Acid sulfate soils occur mainly in the tropics, where over 7.5 million ha are affected (Kawalec, 1973). In the Central Plains region of Thailand there are approximately 800,000 ha of acid sulfate soils, of which about 95% is cultivated in rice (Charoenchamratcheep et al., 1982).

Acid sulfate soils are formed in coastal regions of the world where large quantities of pyrite ( $\text{FeS}_2$ ) accumulate in intertidal sediments. Pyrite accumulation in these sediments is a result of anaerobic conditions, which causes  $\text{SO}_4^{2-}$  from seawater to be reduced to  $\text{S}^{2-}$  and  $\text{Fe}^{3+}$  from ferric oxides to be reduced to  $\text{Fe}^{2+}$ . A large part of the alkalinity formed during sulfate reduction is flushed from the sediments by tidal action, leading to a potentially acid soil. If these soils are aerated, either by natural or artificial drainage, then pyrite is oxidized, releasing  $\text{H}_2\text{SO}_4$  acid and Fe. The acidity resulting from this process causes soil physico-chemical conditions which are detrimental to plant growth. For more information on the genesis of the acid sulfate soils of Thailand see Van Breemen (1976).

Satawathananont (1986) found that the following problems have been attributed to decreased yields of rice grown on acid sulfate soils; (1) adverse effects of  $\text{H}^+$ , (2) Al toxicity, (3) Fe toxicity, (4) sulfide toxicity, (5) Electrolyte stress, (6) adverse effects of  $\text{CO}_2$  and organic and inorganic acids, (7) P deficiency, (8) low base status, and (9) impaired microbial activities.

The objective of this study was to determine the effects of soil physio-chemical parameters on rice growth in acid sulfate soils.

## METHODS AND MATERIALS

The results reported in this chapter were obtained from a field study conducted on 134 acid sulfate soils in the Central Plains Region of Thailand and from a growth chamber study on 30 of the same soils. The methods used in these two experiments are given elsewhere (chapter two).

In addition to these experiments, a micronutrient fertility trial was carried out under greenhouse conditions. Bulk soil samples from the Bangkok, Sena, Rangsit and Rangsit very acid phase (RVAP) series were collected during the dry season in 1984. The Bangkok soil is a non-acid marine soil and the other three are acid sulfate soils. Kevie and Yenmanas (1972) grouped the soils of the Bangkok Plain into four suitability classes, based on productivity and soil mapping units. These classes (P-I, P-II, P-III, and P-IV) indicate the relative limitations on rice production due to acidity, with P-I soils having no limitations to rice production and P-IV soils having a high limitation for rice production due to extreme acidity. The Bangkok soil (Typic Tropaquept) was chosen as a representative soil from the P-I suitability class, the Sena soil (Sulfic Tropaquept) for P-II, the Rangsit soil (Sulfic Tropaquept) for P-III, and the RVAP soil (Sulfic Tropaquept) for the P-IV.

After the soils were collected, they were air dried and ground to pass a 20 mesh sieve. The RVAP sample was split and half of this soil was mixed with the equivalent of ten tons of marl per ha. Two kg of each soil (ie - Bangkok, Sena, Rangsit, RVAP, and RVAP+marl) were then weighed into clay pots lined with plastic bags. The water contents were then adjusted to around 60% of saturation with distilled water and the

soils were allowed to incubate aerobically for 42 d. At this time four seeds of R.D. 23 rice were planted into each pot and the soils were fertilized with N, P, and K ( $75 \text{ mg kg}^{-1}$  soil) as  $(\text{NH}_4)_2\text{HPO}_4$ , KCl, and urea. One week later (two to three leaf stage) micronutrient applications were made and the soils were flooded until harvest. The treatments were; (1)  $5.1 \text{ kg B ha}^{-1}$  equivalent as solubor (20% B), (2)  $1.6 \text{ kg Cu ha}^{-1}$  as copper chelate (13% Cu), (3)  $8.3 \text{ kg Fe ha}^{-1}$  as iron chelate (14% Fe), (4)  $3.5 \text{ kg Mn ha}^{-1}$  as Mn chelate (12% Mn), (5)  $0.3 \text{ kg Mo ha}^{-1}$  as sodium molybdate (39% Mo), (6)  $400 \text{ kg Si ha}^{-1}$  as sodium silicate (23% Si), (7)  $7.3 \text{ kg Zn ha}^{-1}$  as Zn chelate (14% Zn), and (8) control. There were three replications (pots) per treatment in a randomized block design. Urea applications ( $75 \text{ mg N kg}^{-1}$  soil) were repeated at panicle initiation (P.I.). Nutrient applications were made by dissolving the appropriate amount of each amendment in water and pipetting 20 ml of solution on the moist soil, with the exception of the Si treatment and the urea application at P.I. The Si treatment was accomplished by evenly distributing the sodium silicate on the soil surface. The midseason urea application was made by injection into the soil (2-3 cm deep) with a hypodermic needle.

There were 10 to 18 panicle bearing stems in each pot at maturity. The pots were harvested and yields were determined on a hulled rice basis, corrected for water content. Least significant differences were used to compare treatment means within each soil group after ANOVA showed a significant treatment effect for the Bangkok, RVAP, and RVAP+marl soils.

## RESULTS AND DISCUSSION

The soil variables measured in the field and growth chamber experiments and their abbreviations to be used in the discussion are listed in Table 1. The simple linear correlation coefficients between these parameters and growth indices that were significant at the .0001 level are shown in Table 2.

Dry matter production in the growth chamber experiment is plotted as a function of  $E'-Fe$  in Fig. 1. These data indicate the deleterious effects of disproportionately high  $Fe^{2+}$  activities on the growth of rice in acid sulfate soils. Although  $Fe^{2+}$  activities were also negatively correlated with dry matter production (Table 2), the effect of  $E'-Fe$  was much stronger, indicating the ratio of  $Fe^{2+}$  activity to that of the other divalent metals was more important than  $Fe^{2+}$  alone. This was also shown to be the case for Fe uptake (chapter two). Fe stress in rice growing on acid sulfate soils was also reported by Nhung and Ponnamperna (1966) and Tanaka and Navasero (1966).

Dry matter production is plotted as a function of  $E'-Ca$  in Figure 2. Dry matter production was positively correlated with  $E'-Ca$ , indicating that these soils may be deficient in Ca. Attanandana et al. (1982) also showed positive correlations between Ca in soil solution and rice growth on acid sulfate soils. Several researchers have indicated that Ca may play an important role in Fe toxicity in rice (Benckiser et al., 1984; Howeler, 1973; Otto et al., 1983). These researchers have usually indicated that Fe toxicity is a result of a multiple nutritional stress and not simply the result of excess Fe. These findings are easily explained when activity ratios are employed. When  $E'-Fe$  is high,



Table 1 - Soil parameters measured in the growth chamber and field studies and their abbreviations.

<u>Variable measured</u>	<u>Abbreviation</u>
interstitial pH	pH
soil pe	pe
pe + pH	pe + pH
electrical conductivity (siemens/l)	E.C.
ionic strength (moles/l)	I.S.
-log Fe <sup>2+</sup> activity	pFe <sup>2+</sup>
-log Mn <sup>2+</sup> activity	pMn <sup>2+</sup>
-log Mg <sup>2+</sup> activity	pMg <sup>2+</sup>
-log Cu <sup>2+</sup> activity	pCu <sup>2+</sup>
-log Ca <sup>2+</sup> activity	pCa <sup>2+</sup>
-log Al <sup>3+</sup> activity	pAl <sup>3+</sup>
-log B(OH) <sub>4</sub> <sup>-</sup> activity	pB(OH) <sub>4</sub> <sup>-</sup>
-log Zn <sup>2+</sup> activity	pZn <sup>2+</sup>
-log MoO <sub>4</sub> <sup>2-</sup> activity	pMoO <sub>4</sub> <sup>2-</sup>
-log Si(OH) <sub>4</sub> <sup>0</sup> activity	pSi(OH) <sub>4</sub> <sup>0</sup>
-log Cl <sup>-</sup> activity	pCl <sup>-</sup>
-log K <sup>+</sup> activity	pK <sup>+</sup>
-log Na <sup>+</sup> activity	pNa <sup>+</sup>
-log CO <sub>3</sub> <sup>2-</sup> activity	pCO <sub>3</sub> <sup>2-</sup>
-log PO <sub>4</sub> <sup>3-</sup> activity	pPO <sub>4</sub> <sup>3-</sup>
exchangeable Al (cmoles/kg)	ExAl
exchangeable Fe (cmoles/kg)	ExFe
exchangeable Mn (cmoles/kg)	ExMn
exchangeable Ca (cmoles/kg)	ExCa
exchangeable Mg (cmoles/kg)	ExMg
Al saturation of CEC (%)	Alsat
divalent charge fraction in soil solution due to Fe <sup>2+</sup>	E'-Fe
divalent charge fraction in soil solution due to Mn <sup>2+</sup>	E'-Mn
divalent charge fraction in soil solution due to Ca <sup>2+</sup>	E'-Ca
divalent charge fraction in soil solution due to Mg <sup>2+</sup>	E'-Mg
divalent charge fraction in soil solution due to Zn <sup>2+</sup>	E'-Zn
divalent charge fraction in soil solution due to Cu <sup>2+</sup>	E'-Cu
divalent charge fraction on CEC due to Fe	E-Fe
divalent charge fraction on CEC due to Ca	E-Ca
divalent charge fraction on CEC due to Mg	E-Mg
divalent charge fraction on CEC due to Mn	E-Mn

Table 2 - Significant simple correlation coefficients (.0001 level) between soil parameters and dry matter production in the growth chamber study and reported yields in the field study.

<u>Soil parameter</u>	<u>Dry matter production (n = 49)</u>	<u>Yield (n = 110)</u>
E'-Fe	-.70	-.38
pCO <sub>3</sub> <sup>2-</sup>	-.68	-.61
pPO <sub>4</sub> <sup>3-</sup>	-.66	-.64
pH	.64	.64
pAl <sup>3+</sup>	.57	.63
pCa <sup>2+</sup>	-.57	
pB(OH) <sub>4</sub> <sup>-</sup>	-.56	-.60
ExCa	.56	.44
pFe <sup>2+</sup>	.52	
Alsat		-.58
pCu <sup>2+</sup>		.49
pe		-.47
ExMg		.44
pZn <sup>2+</sup>		.44

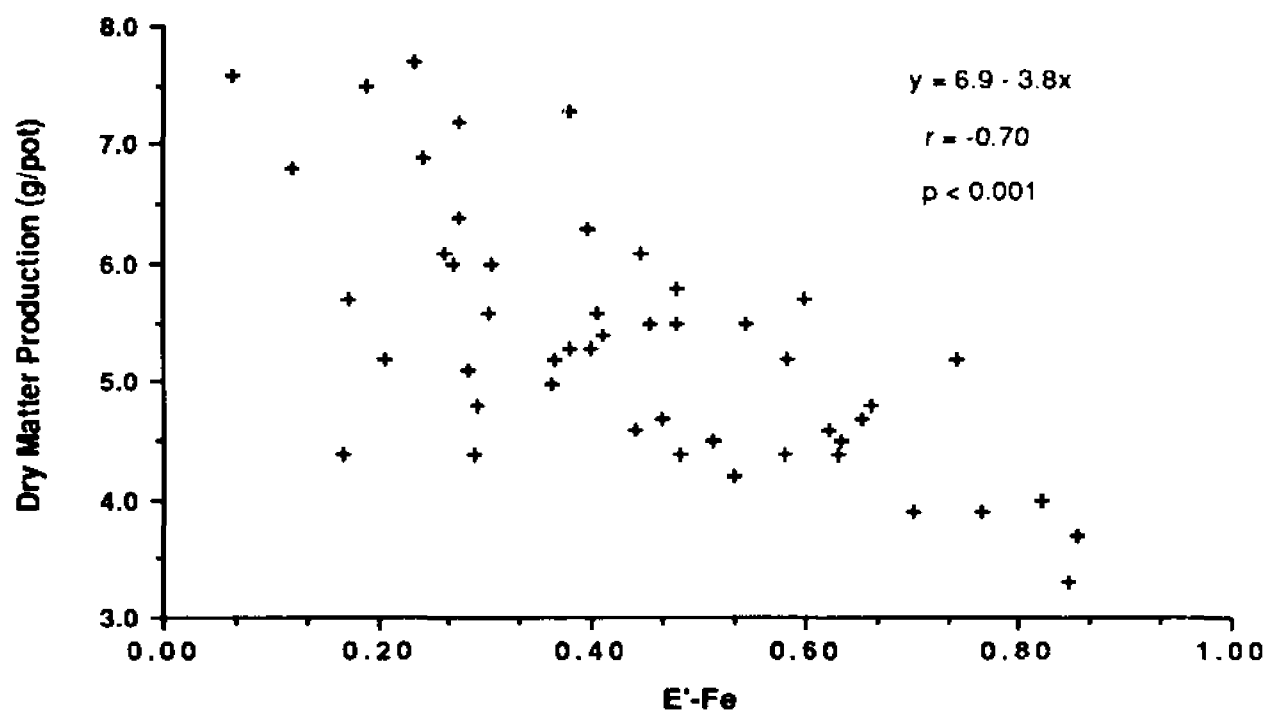


Fig. 1. The relationship between dry matter production and  $E'-Fe$  in the growth chamber study ( $n = 49$ ).

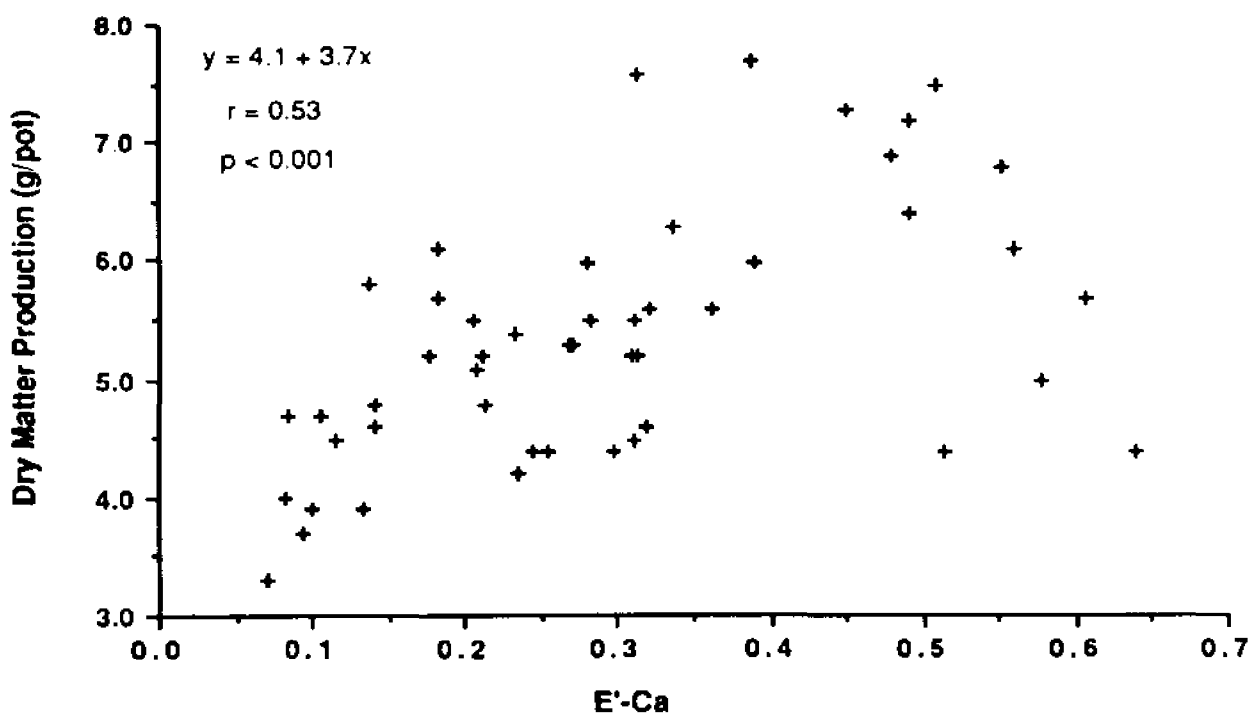


Fig. 2. The relationship between dry matter production and  $E'-Ca$  in the growth chamber study ( $n = 49$ ).

then  $E^+-Ca$  is low and Fe uptake will occur at the expense of Ca uptake. This may not only result in Fe toxicity, but in Ca deficiency as well.

Many researchers studying mineral imbalances in rice have found that when there is a deficiency of one nutrient, then uptake of other nutrients with the same charge is increased, while uptake of nutrients with different charges decreases. Westfall et al. (1973) showed that rice plants suffering from N deficiency had lower Ca and Mg contents than their fertilized counterparts. Yoshida and Castaneda (1969) showed that Na uptake increased in K-deficient rice. Honma and Hirata (1978) found that cadmium uptake increased in Zn-deficient rice. Gangwar and Mann (1972), Sedberry et al. (1971) and Yoshida et al. (1971) showed that Zn deficient rice had higher Fe and Mn contents than plants that had received Zn fertilizer. Moore and Patrick (1987) found that Zn-deficient rice plants had significantly higher concentrations of Ca, Mg, and Cu, while they had lower concentrations of K. They suggested that this may be due to increased production of charge specific carriers in the roots of rice suffering from a nutrient deficiency. If carrier production is metabolically linked, then Ca-deficient rice may be much more sensitive to Fe toxicity than healthy rice, due to the production of divalently charged carriers.

Dry matter production is plotted as a function of  $pAl^{3+}$  in Fig. 3. The highly significant correlation shown by these data is indicative of the adverse effects of Al on rice growth. Although high  $Al^{3+}$  activities were not always reflected by leaf Al contents, they were found to be negatively correlated with leaf P (chapter five). Interference in P uptake and/or assimilation has been suggested as the mechanism of Al toxicity in rice (Tanaka and Navasero, 1966). Al toxicity in rice

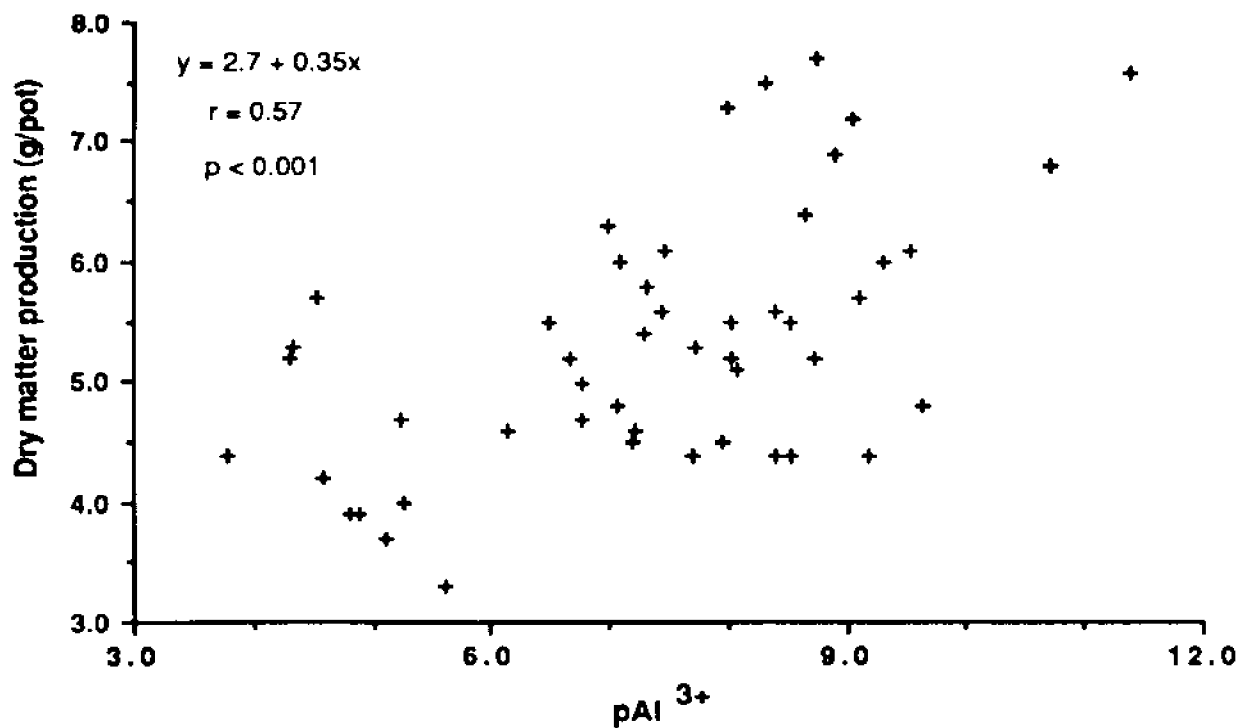


Fig. 3. The relationship between dry matter production and  $Al^{3+}$  activity in the growth chamber study ( $n = 49$ ).

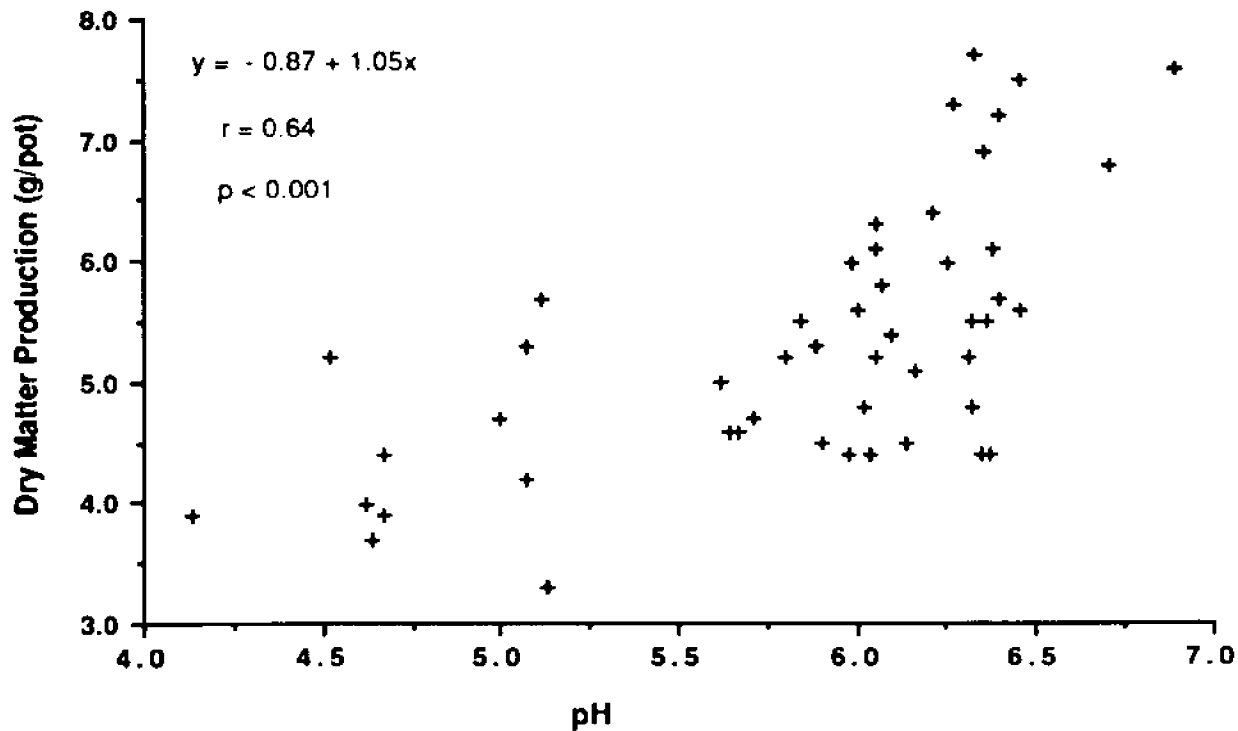


Fig. 4. The relationship between dry matter production and pH in the growth chamber study ( $n = 49$ ).

growing on acid sulfate soils has also been shown by other workers (Jugsujinda et al., 1978; Nhung and Ponnamparuma, 1966).

Dry matter production is plotted as a function of pH in Fig. 4. The highly significant correlation shown by these data illustrates the dominating effect of pH on rice growth in these soils. However, care must be taken when using pH as an indicator of soil productivity in soil testing for acid sulfate soils since it is highly dependent upon the oxidation status of the soil being evaluated. For example, the pH of all 50 soils studied in the growth chamber experiment was within 0.5 units of pH 4.0 prior to flooding and was not significantly correlated with dry matter production or the pH at P.D. (data not shown). Meaningful pH measurements can be attained after the soil has been flooded and reduction has occurred. The author suggests that pH measurements for soil testing purposes should be made by directly inserting a glass electrode into a soil that has been flooded with an excess amount of distilled water for a period of 28 d. Although pH measurements of the soil solution may be more meaningful parameters, the methodology involved is more complex and the necessary equipment to obtain the pore water is often lacking in Third World countries.

Sulfide toxicity has also been reported as a possible constraint to rice growth on acid sulfate soils (Satawathananont, 1986). However, this disorder was not believed to be of importance in the soils investigated in this study. The reasons for this belief were (1) free sulfide concentrations were always below the detection limit of the method employed ( $10^{-7}$  M) and (2) the high levels of  $\text{Fe}^{2+}$  observed in this study would result in  $\text{S}^{2-}$  precipitation as FeS (mackinawite) or  $\text{FeS}_2$  (pyrite), thereby inactivating it. If a small amount of  $\text{S}^{2-}$  were

present in these soils, it would probably be oxidized as it entered the rhizosphere since selection of rice varieties for acid sulfate soils is strongly based on Fe tolerance (ie - oxidizing capability).

Rorison (1973) suggested that Mn toxicity may be a possible constraint on rice growth in acid sulfate soils. However, results of this investigation showed that  $Mn^{2+}$  activity, E'-Mn and leaf Mn content were not related to dry matter production (data not shown). In fact, growth responses to Mn applications have been documented on acid sulfate soils (Nhung and Ponnampetuma, 1966; Ponnampetuma and Solivas, 1980).

Rorison (1973) also suggested that the reduced availability of Mo may effect plant growth on acid sulfate soils. However, no responses to Mo applications were observed in the greenhouse micronutrient fertility trial (Table 3). The only significant response that was observed was that of the Si treatment on the marled RVAP soil.

Response of rice to Si applications were also observed by Okuda and Takahashi (1964). These workers stated that Si responses in rice may be due to decreased Fe toxicity. In culture solutions they showed that the concentration of Fe needed to induce Fe toxicity in the presence of added Si was twice that needed in it's absence. They concluded that the beneficial effects of Si on Fe toxicity were due to an increase in the oxidizing power of the roots, since Si-supplied plants had lower shoot Fe and higher root Fe (mainly as oxides on the surfaces) than their unamended counterparts. This hypothesis could not be tested in this study since leaf metal concentrations were not determined in the greenhouse experiment. It should be noted that Si applications on all of the soils in this study resulted in the floodwater turning black.

Table 3 - Mean rice yields (g/pot) from the micronutrient fertility trial (hulled weight basis, corrected for water content).

Treatment	Bangkok	Sena	Rangsit	RVAP	RVAP+marl†
B	17.22ab	15.39a	11.15a	9.86ab	13.72bc
Control	16.87ab	15.44a	11.03a	10.31ab	12.91bc
Cu	17.08ab	15.24a	11.02a	11.05ab	14.51b
Fe	19.27a	14.30a	10.74a	10.54ab	14.55b
Mn	17.56ab	14.86a	12.10a	10.33ab	14.96b
Mo	16.12b	13.72a	10.81a	10.89ab	12.08c
Si	18.62ab	15.51a	12.08a	12.14a	18.14a
Zn	17.34ab	14.93a	10.77a	9.03b	13.96bc

† - Means with the same letter within a column are not significantly different.



This color change was accompanied by an increase in floodwater pH of roughly one unit over that of the other treatments (data not shown).

As stated in the methods and materials section, the midseason N and P application in the greenhouse study was made by injection. This was done in order to avoid N loss by nitrification-denitrification reactions. Prior to the midseason fertilizer application the plants growing in the RVAP soil were approximately 10 cm taller than their marled counterparts. This difference in growth was probably due to increased denitrification in the marled soil due to more favorable conditions for microorganisms, resulting in lower N fertilizer efficiency. Within a few days of the midseason fertilization, the plants growing in the marled RVAP soil were noticeably taller than those in the unmarled soil. These observations indicate that extra precautions, such as deep-placement of fertilizer N, may be needed in order to minimize N loss when acid sulfate soils are limed.

#### MODELLING RICE GROWTH

In order to delineate the roles played by the various physico-chemical agents that appear to be limiting rice growth on acid sulfate soils, growth indices were modelled using multiple regression. Whereas simple correlation measures only the interactions between individual variables, more intricate associations may be determined from statistical analyses which evaluate relationships between many variables. Therefore, a stepwise regression program was conducted to determine the best multiple regression equation relating dry matter production in the growth chamber experiment and yields in the field study to the soil properties measured. The maximum  $R^2$  improvement

technique (MAXR) was used for this analysis (SAS, 1985), with the upper limit of independent variables entering into the model being set at seven.

The preliminary results of this analysis showed that two of the most important variables relating to dry matter production and yields were  $\text{pCO}_3^{2-}$  and  $\text{pPO}_4^{3-}$ . However, when these parameters were included in the analysis, it resulted in negative regression coefficients for pH and positive regression coefficients for  $\text{E}'\text{-Fe}$ , which would appear to contradict the effects of these parameters on rice growth. Since  $\text{pCO}_3^{2-}$  and  $\text{pPO}_4^{3-}$  were both calculated from and were highly correlated to pH ( $r = -.98$  and  $-.99$ , respectively), the problem was one of multicollinearity. Therefore, they were omitted from the analysis in order to obtain a model that more accurately reflects the true nature of these soils.

The results of the final analysis showed that the best three variable regression equation for dry matter production in the growth chamber study included pH, ionic strength, and  $\text{E}'\text{-Fe}$ . No other variables met the 0.15 significance level for entry into the model. The regression coefficients (B values), F values and significance levels of these parameters are given in Table 4. These data demonstrate that the divalent charge fraction in the soil solution attributable to Fe, ionic strength and pH of the soil solution accounted for 65% of the variation in dry matter production. This would indicate that salinity, acidity and Fe stress were the dominant factors influencing rice growth on these soils. It should be noted that Fe stress not only involves high  $\text{Fe}^{2+}$  activities, but also a low base status. Similarly, since pH has an intimate association with the Al and P status of the soil, it probably

Table 4 - Summary of stepwise regression analysis for dry matter production in the growth chamber study and reported yields in the field experiment.

variable	$\beta$ value	partial R <sup>2</sup>	model R <sup>2</sup>	F value	prob>F
<b>GROWTH CHAMBER STUDY</b>					
<u>Dependent variable = dry matter production†</u>					
intercept	3.40				
pH	0.58	0.53	0.53	54.2	0.0001
I.S.	-39.42	0.05	0.58	5.3	0.0256
E'-Fe	-2.81	0.07	0.65	9.3	0.0038
<b>FIELD STUDY</b>					
<u>Dependent variable = reported yield‡</u>					
intercept	-505.5				
pH	656.3	0.38	0.41	67.9	0.0001
E'-Fe	-1667.3	0.03	0.44	6.1	0.0151

† degrees of freedom = 49

‡ degrees of freedom = 108

reflects the effects of these variables on growth. Although ionic strength was not significantly correlated to dry matter production alone, this analysis indicates that when the plants are suffering from acidity and/or Fe stress, then the detrimental impact of ionic strength comes into play.

Results from the field study indicated that pH and  $E'-Fe$  comprised the best two variable equation for yield (Table 4). No other variables met the 0.15 significance level for entry into the model. These findings support those observed in the growth chamber study. Evidently, ionic strength played a lesser role in the field study than in the growth chamber study. This was probably due to more intense oxidation of the soils prior to the growth chamber study than what occurs under field conditions. The potential acid sulfate soils, which are normally located in coastal areas, are usually more saline than their inland counterparts. Under field conditions these soils probably experience wetter conditions and thus produce less acidity from oxidation than those in the growth chamber study. Therefore, the plants growing on potential acid sulfate soils in the field probably encounter only a slight salinity stress which they are able to overcome. However, when these soils are oxidized (as in the growth chamber study), the plants are subjected to dual stresses from both acidity and salinity.

Predicted and observed dry matter production in the growth chamber study and yields from the field study are plotted in Figs. 5 and 6, respectively. These data indicate that the models predicted the observed growth indices better under low growth situations. Under conditions of high growth the models probably break down because the pH,

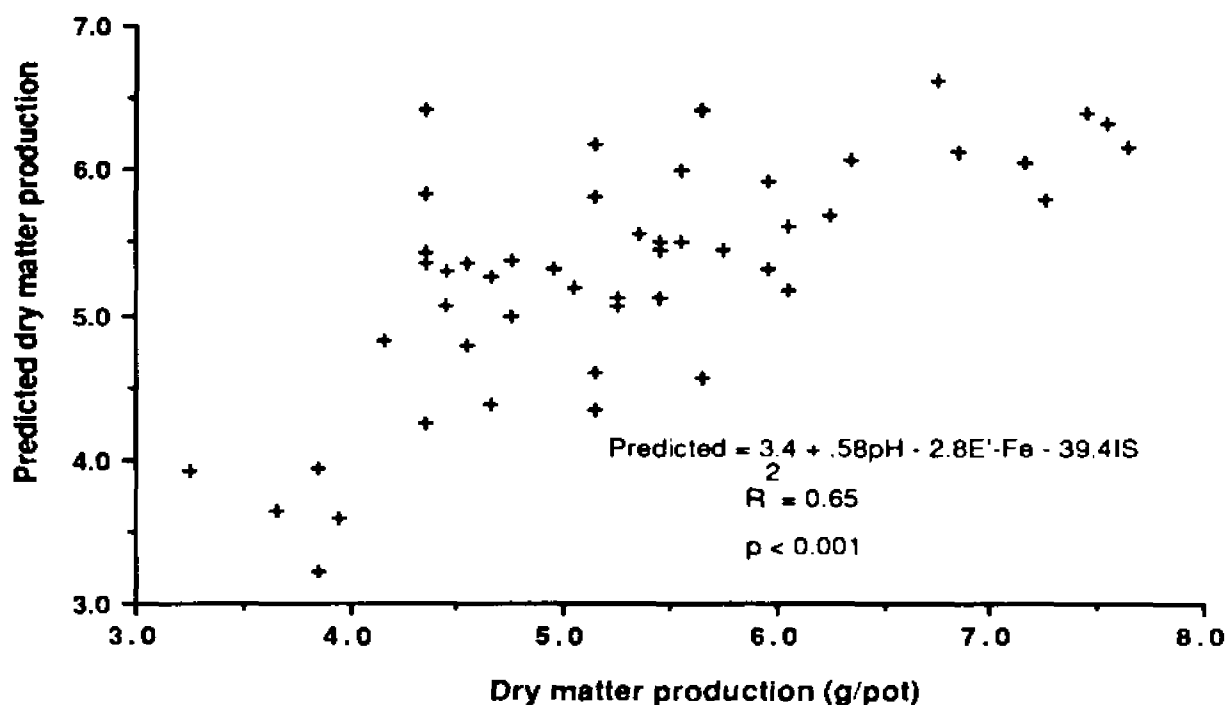


Fig. 5. The relationship between predicted and observed dry matter production in the growth chamber study (n = 49).

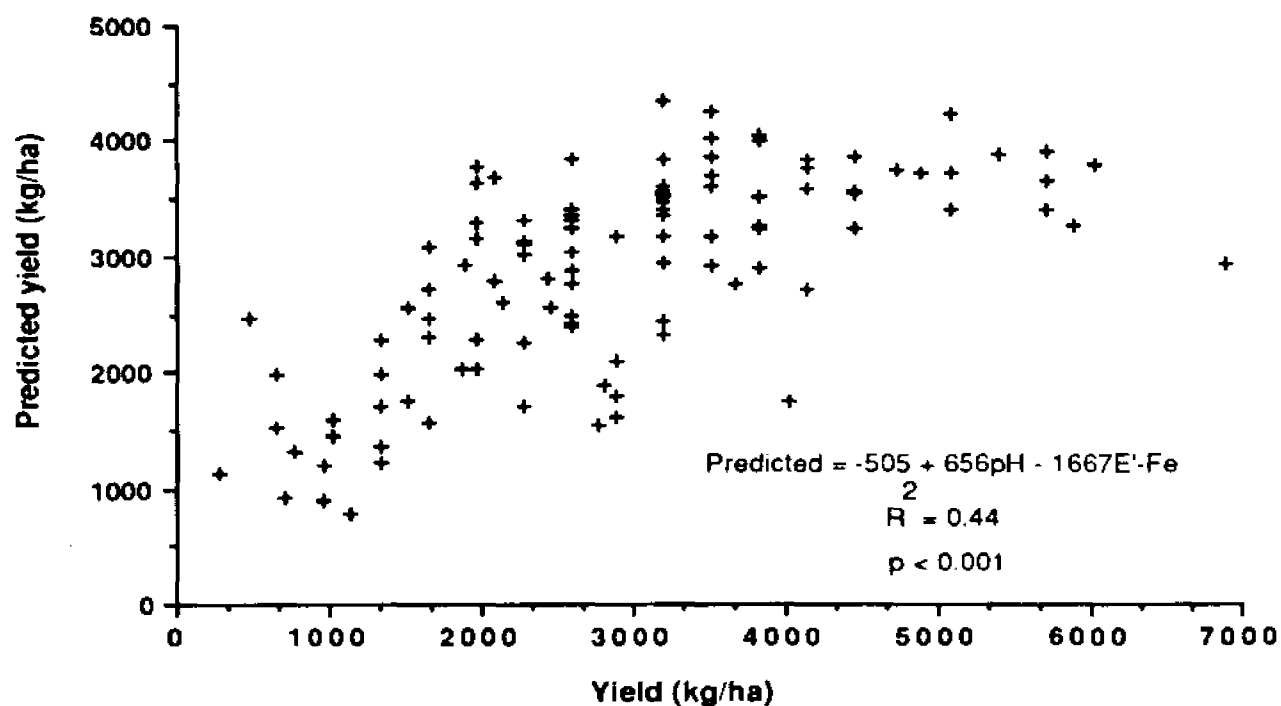


Fig. 6. The relationship between predicted and reported yields in the field study (n = 110).

salinity and Fe stress are no longer governing growth, whereas other variables such as N nutrition may become important.

### CONCLUSIONS

Simple and multiple correlation techniques were employed to determine the main soil physico-chemical parameters affecting rice growth on acid sulfate soils. Simple linear correlations indicated that growth was positively correlated with the activities of  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{B}(\text{OH})_4^-$ ,  $\text{Ca}^{2+}$ , pH, exchangeable Ca, exchangeable Mg and  $\text{E}'\text{-Ca}$ . Growth was found to be negatively correlated with the activities of  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ , pe, % Al saturation of the CEC and  $\text{E}'\text{-Fe}$ . A micronutrient fertility trial also indicated that Si deficiencies may be occurring on limed acid sulfate soils.

Results from multiple regression analysis indicated that  $\text{E}'\text{-Fe}$ , pH and ionic strength provided the best 3 variable model describing dry matter production in the growth chamber study. Whereas in the field study the best 2 variable model describing reported yields included pH and  $\text{E}'\text{-Fe}$ . In light of these findings, the most important constraints to rice growth on acid sulfate soils were believed to be (1) Fe stress - which is due to the combined effects of Fe toxicity as well as deficiencies of other divalent cations, and (2) acidity - which includes the combined effects of low pH, Al stress and P deficiency.

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## Summary and Conclusions

## SUMMARY AND CONCLUSIONS

Metal availability and uptake by rice was evaluated in 134 flooded acid sulfate soils in the Central Plains region of Thailand and in 50 of the same soils in a growth chamber study. Soil and plant metal analyses were conducted at the panicle differentiation stage of growth in both studies and in the soil prior to planting in the growth chamber study. Metal activities were determined from free metal concentrations using GEOCHEM. Exchangeable metals were determined from sodium acetate extracts buffered to the soil pH.

The results of this study indicated that  $\text{Fe}^{2+}$  activities are seldom in equilibrium with pure Fe solid phases in these soils. This was believed to be due to (1) transient redox conditions, (2) the presence of ill-defined ferric oxides or hydroxides, and/or (3) cation exchange reactions. Equilibria calculations also indicated that the soils were undersaturated with respect to most Ca, Mg, and Mn solid phases, and their activities in soil solution were believed to be controlled by cation exchange reactions.  $\text{Al}^{3+}$  activities were very pH dependent and appeared to be controlled by kurbanite at low pH and amorphous  $\text{Al}(\text{OH})_3$  at high pH. However, cation exchange was also suspected as an important governing mechanism of  $\text{Al}^{3+}$  in solution.  $\text{Zn}^{2+}$  activities were also very pH dependant, with franklinite being the suspected stable phase of this metal.  $\text{Cu}^{2+}$  activities were positively correlated to pe and indicated supersaturation with respect to cuprous ferrite in most of the soils studied.  $\text{MoO}_4^{2-}$  activities were positively correlated to pH and may have been controlled by wulfenite.  $\text{B}(\text{OH})_3^0$  was found to be the dominant species of B in solution and was highly correlated to ionic strength.

Leaf analysis indicated that although Fe uptake was significantly correlated with  $\text{Fe}^{2+}$  activity, a better relationship existed between uptake and  $E'-\text{Fe}$  (the divalent charge fraction in the soil solution due to  $\text{Fe}^{2+}$ ). Ca, Mg, and Mn uptake was also found to be more closely related to  $E'-\text{Ca}$ ,  $E'-\text{Mg}$  and  $E'-\text{Mn}$ , respectively, than to the activities of these ions. These results indicate that activity ratios may be better availability indices than ion activities in many situations. This is probably due to competitive inhibition for uptake sites on the roots. Although Al uptake was not correlated to  $\text{Al}^{3+}$  activities, P uptake was. This phenomenon was believed to be due to P precipitation by Al, since most of the soils studied were supersaturated with respect to variscite. Significant relationships were also found between Cu and Mo uptake and the activities of  $\text{Cu}^{2+}$  and  $\text{MoO}_4^{2-}$ . However, Zn uptake was not significantly correlated with Zn activity. Plant analysis also indicated that Fe and Al toxicities and Ca and Mg deficiencies in rice may be occurring on these soils. Results from the micronutrient fertility trial indicated that Si deficiencies may be occurring on limed acid sulfate soils.

Many of the soil parameters investigated in this study were significantly correlated to dry matter production in the growth chamber experiment and yields in the field study. However, multiple regression analyses revealed that the two most important variables relating to rice growth on these soils were  $E'-\text{Fe}$  and pH. While  $E'-\text{Fe}$  was considered to be a good measure of Fe stress (Fe toxicity combined with deficiencies of basic cations), pH measurements reflected the availability of many nutrients and toxins, such as P and Al.

## Appendix

## Rice Production in Thailand

There are two seasons for rice production in the Central Plains of Thailand. The first begins around January and continues until May. Since this is during the dry season, floodwater is provided by irrigation from rivers or small canals locally known as klongs. Although rice yields in this season are generally greater due to an increased ability to regulate floodwater depths, very few of the farmers surveyed in this study were able to utilize this growing season because their farms were too distant from surface waters. Most rice varieties grown during this season were non-photoperiod sensitive. These are improved varieties that have been developed from strains of rice from IRRI.

The monsoon crop is planted from June to August and is harvested around December. Over half of the varieties sampled during this season were photoperiod sensitive, native varieties. The popularity of these varieties arises from their ability to withstand harsh growing conditions. Many of them were deepwater varieties which could grow at a rate necessary to keep up with the monsoon floods. Floodwater depths in many of the fields during this season were over 1 m, with some approaching 2 m.

The size of the farms sampled in this study varied from 0.5 to 40 ha, with an average of about 3 ha. Traditionally, the fields were worked with water buffalo. However, in the past 10 years the use of water buffalo has declined in favor of the small, hand-held, gas-powered tractors which are currently being used (Plate 1). These machines require little fuel and are relatively maintenance free. They are also used as irrigation pumps during the dry season, as shown in Plate 2.

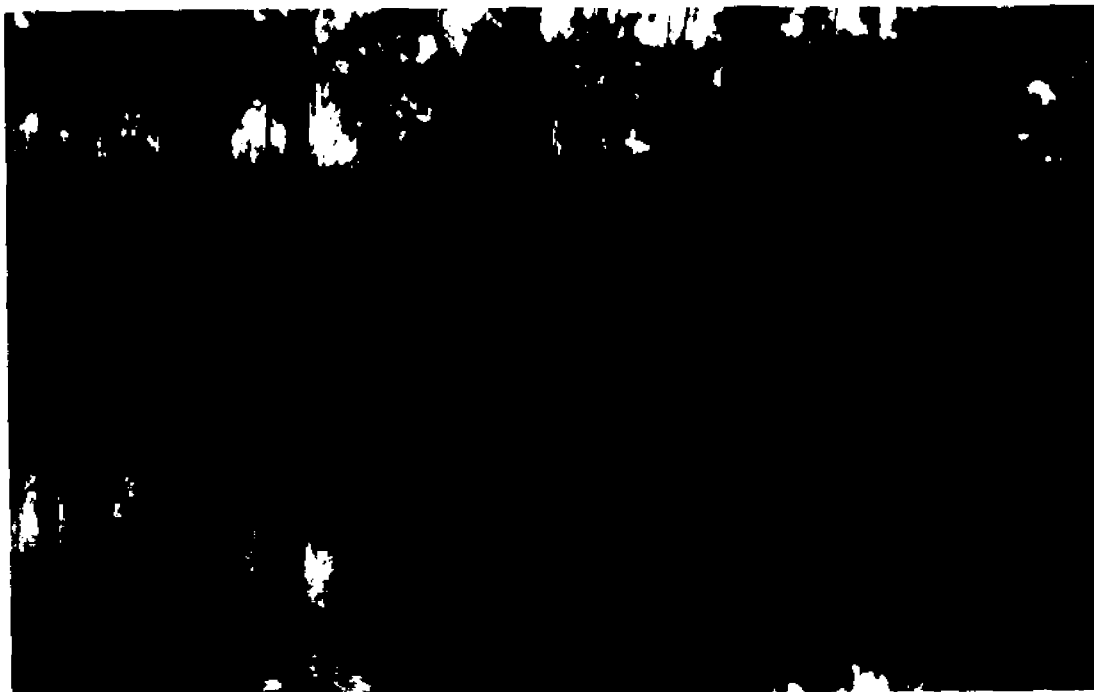


Plate 1. Hand-held tractor used for rice production in Thailand, locally referred to as kwai lek (iron buffalo).



Plate 2. A tractor being used for an irrigation pump during the dry season.

This transformation in technology has resulted in increased consumption of water buffalo meat, causing a decrease in the population of these animals in Thailand from 45 million to 10 million in the past decade.

The two methods of planting rice in Thailand are (1) broadcasting germinated seed and (2) transplanting. Although the majority of the fields sampled in this study were planted by the first method, over 40 percent were transplanted.

In order to germinate the seeds for broadcasting, the farmers place them in burlap bags which are then submerged in a waterbody such as a klong. After 2 or 3 days of submergence, the seeds are removed and broadcast by hand onto the field, which has been puddled and is saturated with water.

For transplanted rice, the farmers start the plants in highly fertilized seedbeds such as that shown in Plate 3. Due to the small size of these nursery beds, the time of flooding and floodwater depth can be controlled so as to maximize growth. Shortly after the onset of tillering (4 weeks) the plants are carefully pulled up and the soil is washed from the roots. The tips of the leaves are then cut off so that all of the plants are roughly the same height. It was the author's opinion that this was done in order to decrease lodging, however, one of the farmers conducting this practice stated that it was done to allow the roots to "breathe easier". After the leaf tips have been cut, bundles of the young plants are carried to the main field (which is flooded) and planted 4 to 5 cm deep in rows. The amount of labor required for this procedure is tremendous. Therefore, fields are normally planted by groups of people as shown in Plate 4.



Plate 3. Seedbed used for obtaining seedlings for transplanted rice.



Plate 4. Transplanting rice in the Central Plains of Thailand.



An interesting chemical diagnostic technique utilized by rice farmers in the Central Plains region to determine when the soil pH has increased enough for transplanting involves spitting into the floodwater. Many of the farmers, especially women, chew betelnut for its mild antidepressant effect. When mixed with saliva the juice produced by this nut is blood red. The color is probably derived from an organic dye. When the spit-betelnut juice combination remains red upon contact with the floodwater, the farmers believe the field is too sour (acid) for transplanting. However, when the juice turns black upon contact with the floodwater, it is considered to be a healthy environment for rice. The pH at which this transformation occurs was not determined by the author.

The type of fertilizer used on most of the fields sampled in this study was ammonium phosphate (20-20-0). Applications were made in a one, two or three-way split. Fertilizer application rates varied from 0 to 600 kg ha<sup>-1</sup>, with an average of 170 kg ha<sup>-1</sup>. The fertilizer is broadcast by hand. Two of the farms sampled in this study utilized green manure (source unknown) and four of the farms utilized potassium fertilizer. Sixteen of the farmers' fields sampled had received marl in the past 10 years. The average marl application to these fields was approximately 9 tons ha<sup>-1</sup>.

Pest control in the fields studied varied from nil to excellent. Although many of the farmers questioned utilized pesticides, none used herbicides. Weed control was accomplished by hand. Several of the fields sampled had a severe rat problem. Rats are particularly damaging at the panicle differentiation to booting stage of growth, because they only eat the developing panicle inside each plant. At three different

locations where the rat problem was acute, the farmers had strung 220 volt electric wires around the field, approximately 1 to 2 cm above the floodwater. The dominant predator of rats in these rice fields is the king cobra. However, due to the extremely venomous nature of these reptiles, many farmers have opted to erradicate them from their fields. The primary predator of the cobras in these fields are mongooses, which in turn are preyed upon by water monitor lizards. One particularly annoying pest to farmers working in these fields is the ubiquitous water buffalo leech, which commonly reaches lengths of 12 to 15 cm.

Currently, rice is still harvested by hand in Thailand. After cutting the stems just above the soil surface, the plants are bundled and removed from the field. The grain is then thrashed by hand or with the aid of a water buffaloe tethered to a pole, walking in circles. The grain is then transported (often by boat on the klongs) to granaries where it is sun-dried outdoors on concrete surfaces.

## Vita

Philip Alderson Moore, Jr. was born Feb. 29, 1956 in El Dorado, Arkansas. He enrolled at the University of Arkansas in 1974 and was awarded the Jacob Hartz Scholarship for the outstanding Soil Science student in 1978. He received a B.S. in Soil Science in 1979. After completing an M.S. in Agronomy at the University of Arkansas in 1981, he enrolled at Louisiana State University, where he is presently a candidate for his Doctorate with a major in Marine Sciences and a minor in Agronomy. In 1982 he was awarded a Rockefeller Scholarship for outstanding Marine Science students and in 1983 he received a Fulbright Scholarship to Thailand.

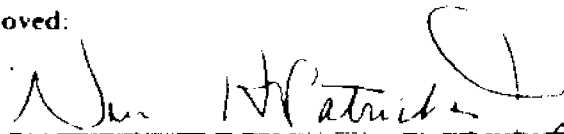
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Philip A. Moore, Jr.

Major Field: Marine Science

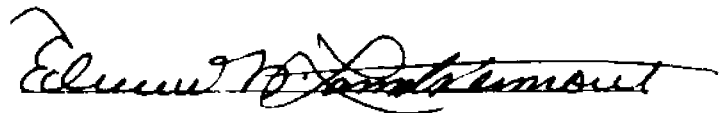
Title of Dissertation: Metal Behavior in Acid Sulfate Soils of Thailand

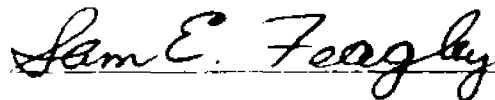
Approved:

  
Major Professor and Chairman

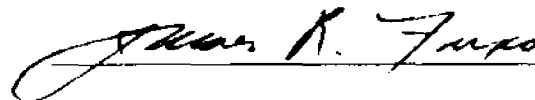
  
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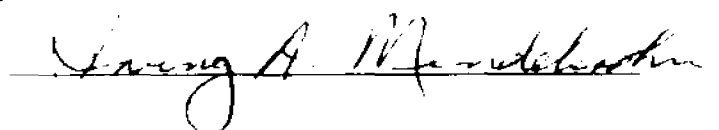
EXAMINING COMMITTEE:











Date of Examination: April 10, 1987